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## Authigenic Carbonates in Methane Seeps from the Norwegian Sea: Mineralogy, Geochemistry, and Genesis

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**Abstract**—Authigenic carbonates in the caldera of an Arctic (72°N) submarine mud volcano with active CH<sub>4</sub>-bearing fluid discharge are formed at the bottom surface during anaerobic microbial methane oxidation. The microbial community consists of specific methane-producing bacteria, which act as methanotrophic ones in conditions of excess methane, and sulfate reducers developing on hydrogen, which is an intermediate product of microbial CH<sub>4</sub> oxidation. Isotopically light carbon ( $\delta^{13}\text{C}_{\text{av}} = -28.9\text{‰}$ ) of carbon dioxide produced during CH<sub>4</sub> oxidation is the main carbonate carbon source. Heavy oxygen isotope ratio ( $\delta^{18}\text{O}_{\text{av}} = 5\text{‰}$ ) in carbonates is inherited from seawater sulfate. A rapid sulfate reduction (up to 12 mg S dm<sup>-3</sup> day<sup>-1</sup>) results in total exhausting of sulfate ion in the upper sediment layer (10 cm). Because of this, carbonates can only be formed in surface sediments near the water–bottom interface. Authigenic carbonates occurring within sediments occur *in situ*. Salinity, as well as CO<sub>3</sub><sup>2-</sup>/Ca and Mg/Ca ratios, correspond to the field of nonmagnesian calcium carbonate precipitation. Calcite is the dominant carbonate mineral in the methane seep caldera, where it occurs in the paragenetic association with barite. The radiocarbon age of carbonates is about 10000 yr.

The investigation of the Earth's crust defluidization is among first priority branches of modern marine geology. Besides other aspects, the problem attracts the attention of researchers due to an occurrence of recent authigenic mineralization and ore formation at fluid discharge sites. For example, authigenic carbonates form at the seafloor during discharge of CH<sub>4</sub>-bearing fluids. Methane represents the main carbon source for these carbonates. Authigenic carbonates remain on the seafloor as the only evidence of methane fluid discharge, thus serving as an important indicator of economic hydrocarbon (oil, gas, and others) resources within the sedimentary sequence beneath the bottom.

Beginning with I.M. Gubkin, Russian scientists noted a close genetic relationship between mud volcanism and hydrocarbon deposits (Ginsburg and Solov'ev, 1994; Kholodov, 1983; and other).

Authigenic carbonates have been intensely studied on land (Chilingar *et al.*, 1971; Kholodov, 1987, 1991, 1999; Taft, 1971). Extensive studies of marine authigenic carbonates started only after the discovery of cold methane seeps on the seafloor (Ivanov *et al.*, 1991; Lein *et al.*, 1989; Suess *et al.*, 1998; Von Rad *et al.*, 1996; Yesikov and Pashkina, 1990).

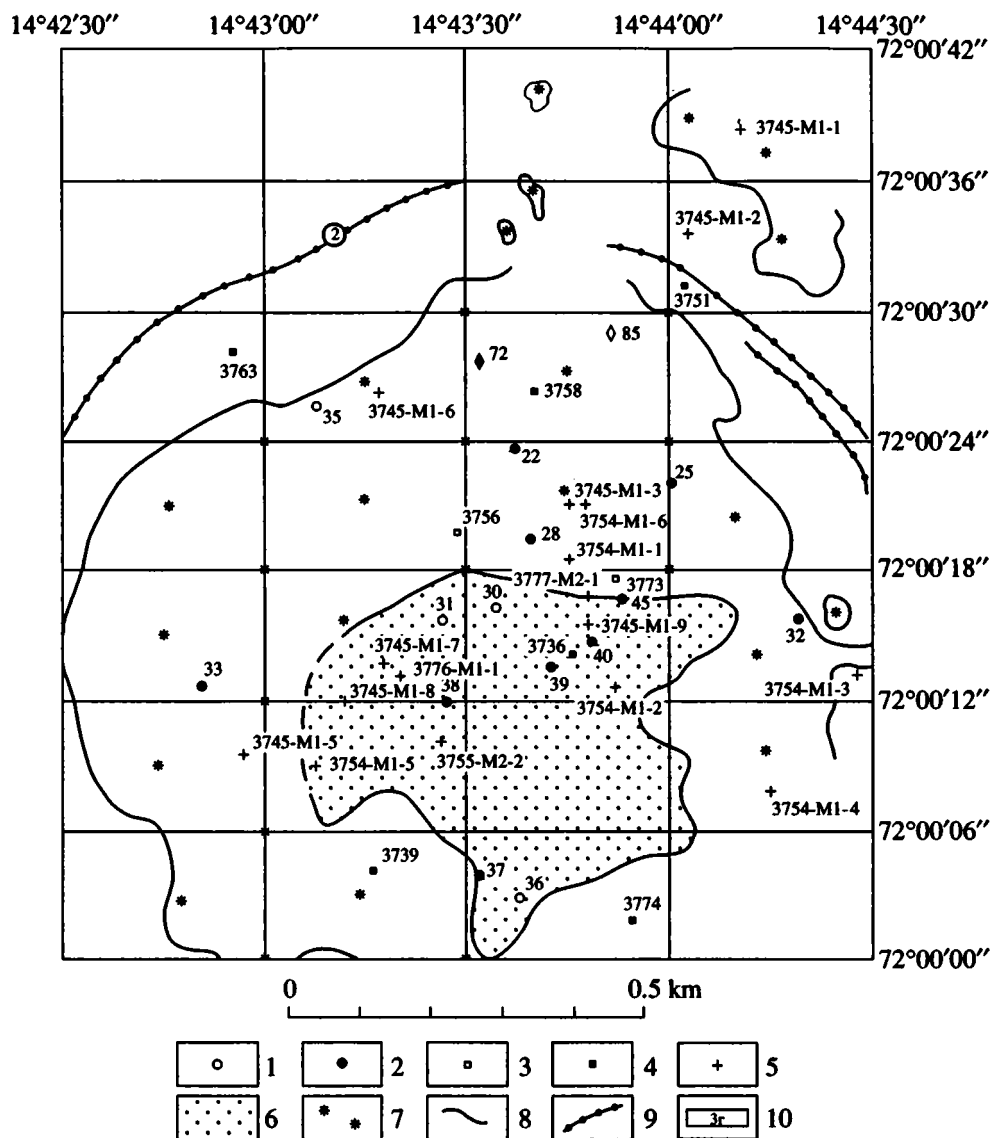
It is well known that precipitation of carbonates depends on physicochemical properties of solutions:

pH, salinity, carbonate alkalinity,  $\Sigma\text{CO}_3^{2-} : \text{Ca}^{2+}$  and  $\text{Mg}^{2+} : \text{Ca}^{2+}$  ratios, temperature, and presence of organic compounds in the reaction zone. Precipitation of carbonates is mainly controlled by the concentration (activity) of carbonate ions formed during organic matter (OM) decay, bacterial sulfate reduction, methane oxidation, and other processes.

In this connection, it is especially interesting to study authigenic carbonates from the active Haakon Mosby methane seep, Norwegian Sea, where biogeochemical processes with participation of several groups of bacteria, as well as sulfur and carbon cycles, were also investigated (Lein *et al.*, 1998; Pimenov *et al.*, 1997; Vogt *et al.*, 1997).

The methane seep is related to activity of the Haakon Mosby mud volcano (HMMV) located at the northeastern margin of the Norwegian Sea (Fig. 1). According to geophysical data, the bottom simulating reflector (BSR) indicates here a zone of methane gas hydrate instability within pre-Holocene glacial sediments at the depth of 850–870 m below seafloor (Minert *et al.*, 1997).

A concentric zonation of CH<sub>4</sub>-bearing sediments is observed in the HMMV caldera (Bogdanov *et al.*, 1999; Lein *et al.*, 1998; Vogt *et al.*, 1997). Black



**Fig. 1.** Location of sampling stations in the HMMV caldera. Stations of sampling by geological instruments, 1996: (1) gas saturated sediments; (2) gas hydrate-bearing sediments; stations of sampling by geological instruments, 1998: (3) gas-saturated sediments; (4) gas hydrate-bearing sediments; (5) surface (0–20 cm) sediments sampled by routine devices of *Mir-1* and *Mir-2* manned submersibles; morphological features of the caldera: (6) central zone, (7) periphery, (8) internal rim (hillock zone); (9) framing rim; (10) sites of authigenic carbonate sampling.

strongly reduced gas-saturated sediments, with a residual  $\text{CH}_4$  content up to 300 ml/l, occur in the central (axial) zone of the caldera, where the maximum heat flow was measured. This zone is surrounded by sediments which contain  $\text{CH}_4$ -gas hydrate. Gas hydrate occurs even in the surface layer of sediments (0–25 cm). The depth of gas hydrate-bearing sediments increases to 50 cm with increasing distance from the caldera center, and it is up to 100 cm or even more at the periphery of the caldera.

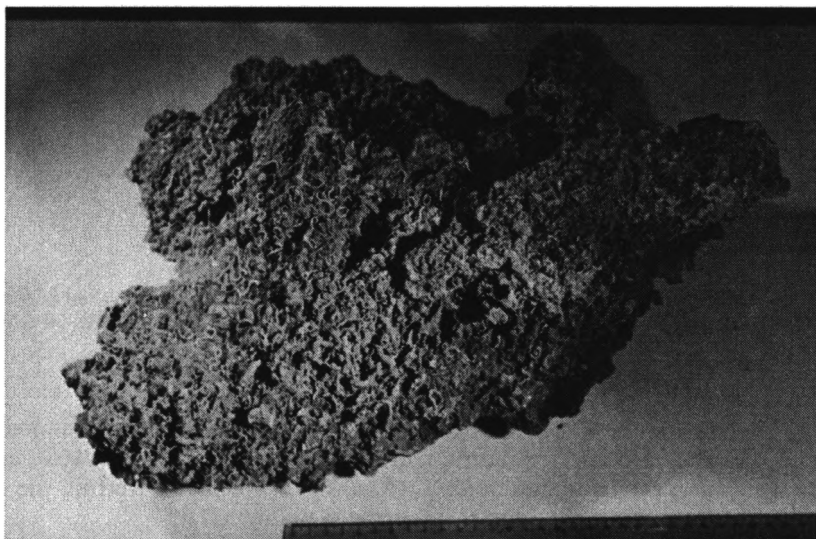
The caldera is separated from outer slopes of the volcano by a rim. A hilly zone occurs in the caldera near the rim. Hillocks are up to 2–3 m high. Summits and slopes of the hillocks are covered with a thin layer

of yellowish brown oxidized sediment. Observations from *Mir-1* and *Mir-2* manned submersibles showed that conical, columnar, and crustlike carbonate build-ups, up to 30 cm high, are widespread on summits and slopes of the hillocks (Fig. 2). Similar buildups with abundant *Pogonophora* overgrowths also occur on a slightly uplifted area in the central part of the caldera (Fig. 3). Along with the carbonate buildups, morphologically variable carbonate bodies were observed within caldera sediments, at depths from 5–10 cm to 40–45 cm below the water–bottom interface (Figs. 4, 5).

The objective of this work is to determine the genesis of various authigenic carbonate precipitates, based on mineralogical and geochemical analyses of carbon-



**Fig. 2.** Bottom surface in the hillock zone with carbonate buildups. Photograph taken from *Mir-1* submersible.



**Fig. 3.** Surface of living coral-shaped carbonate buildup (size  $40 \times 20 \times 15$  cm) at St. 3745-M1-7.

ates and host sediments. We also used data on biogeochemical and geochemical studies of the carbonate precipitation environment.

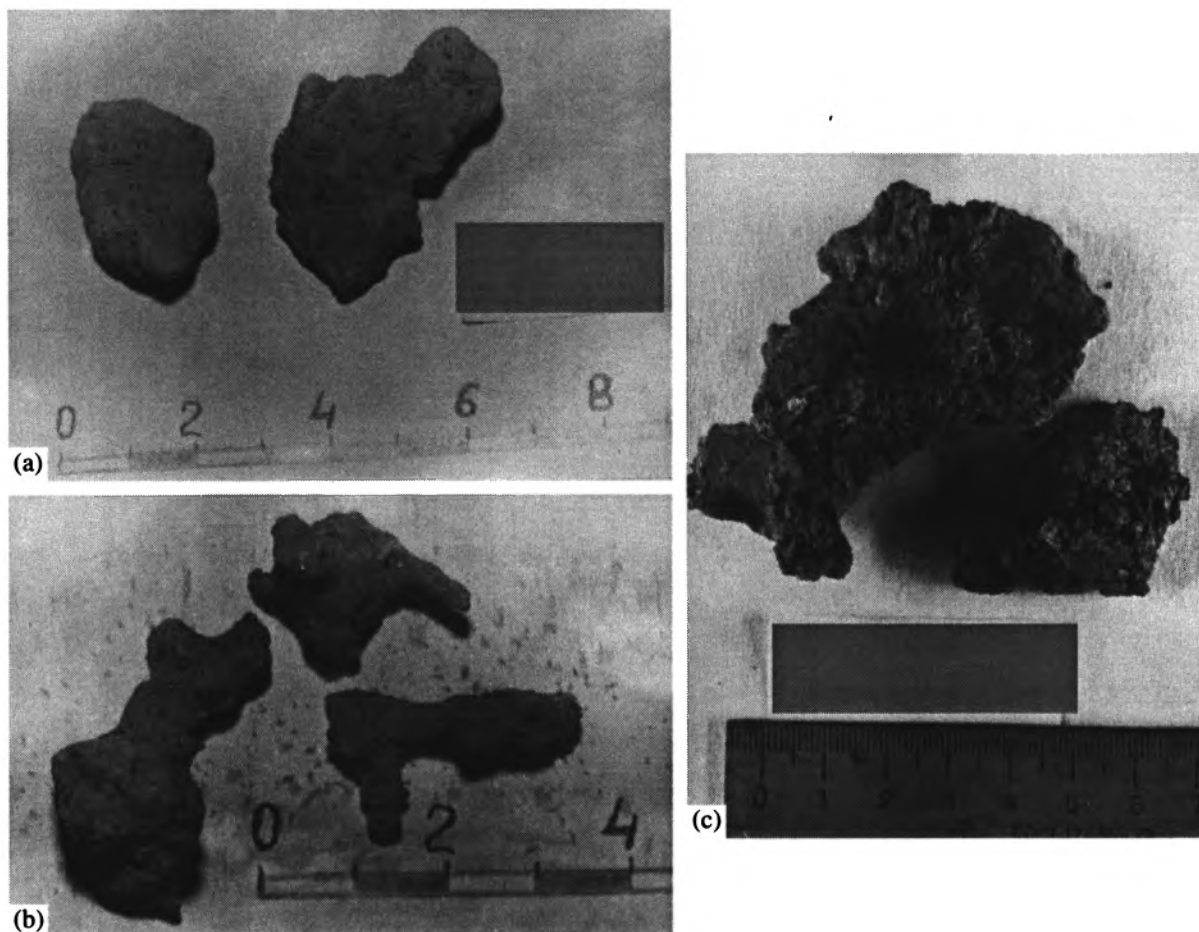
### MATERIALS AND METHODS

Authigenic carbonates and host sediments from the HMMV caldera were sampled using gravity corer and box corer, during Cruise 15 of the R/V *Professor Logachev* (August, 1996), and applying geological samplers installed into *Mir* manned submersibles, during Cruise 40 of the R/V *Akademik Mstislav Keldysh* (July, 1998). Location of the sampling sites is shown in Fig. 1.

The chemical and mineralogical composition of carbonates and host sediments was determined using X-ray fluorescence (bulk composition) and X-ray diffraction techniques. The  $\text{CaCO}_3$  content was determined by measuring carbon dioxide volume extracted from the carbonate during reaction with chloric acid. Pure  $\text{CaCO}_3$  was used as a standard. Precision of the method is 1–2 rel %. The  $\text{C}_{\text{org}}$  content was determined after dissolution of  $\text{CaCO}_3$  with 3M HCl using an AN-7560 express analyser by recording  $\text{CO}_2$  formed during burning ( $T = 900^\circ\text{C}$ ) in  $\text{CO}_2$ -free air stream.

We used routine optical microscopy to study mineralogy, structures, and textures of carbonates in thin sections and immersion specimens. The scanning electron





**Fig. 4.** Morphology of authigenic carbonate bodies from the HMMV caldera. (a) Smooth light-colored bodies with abundant small hollows on the surface (St. 36, interval 30–40 cm); (b) dark gray irregular bodies (St. 32, interval 20–30 cm); (c) fragment of carbonate chimney with hollow channels inside (St. 36, interval 40–42 cm).

microscope JEM-5300 (Japan) with LINK ISIS energy-dispersive spectrometer was also applied. Sample surfaces for the study were smoothed and flattened. Energy-dispersive spectra were commonly obtained for each phase found, and semiquantitative analysis was performed using a JEM-1002 (Japan) transmission electron microscope.

Carbon and oxygen isotopic compositions in carbonates, as well as in organic carbon, were measured using a Micromass-602D mass-spectrometer (England) and MI-1202 V mass-spectrometer (Ukraine). The specimen and standard were preliminarily dissolved with dehydrated orthophosphoric acid in circular vacuum device and were purified by cryogenic method (Esikov, 1980). After the purification, carbon dioxide was soldered into ampules and used for the isotope analysis.

For C–C<sub>org</sub> isotopy, samples were treated by HCl 1 : 4 with heating to remove carbonates. After this, the specimen was burned in a quartz tube with CuO, at the temperature 900°C, using a circular vacuum device. The obtained CO<sub>2</sub> was soldered in ampules and its iso-

topic composition was determined. The CaCO<sub>3</sub> sample MCA-8 with  $\delta^{13}\text{C} = -31.46\text{‰}$  and  $\delta^{18}\text{O} = 16.04\text{‰}$  (Katalog..., 1988) served as the standard. Analytical error is within  $\pm 0.5\text{‰}$ .

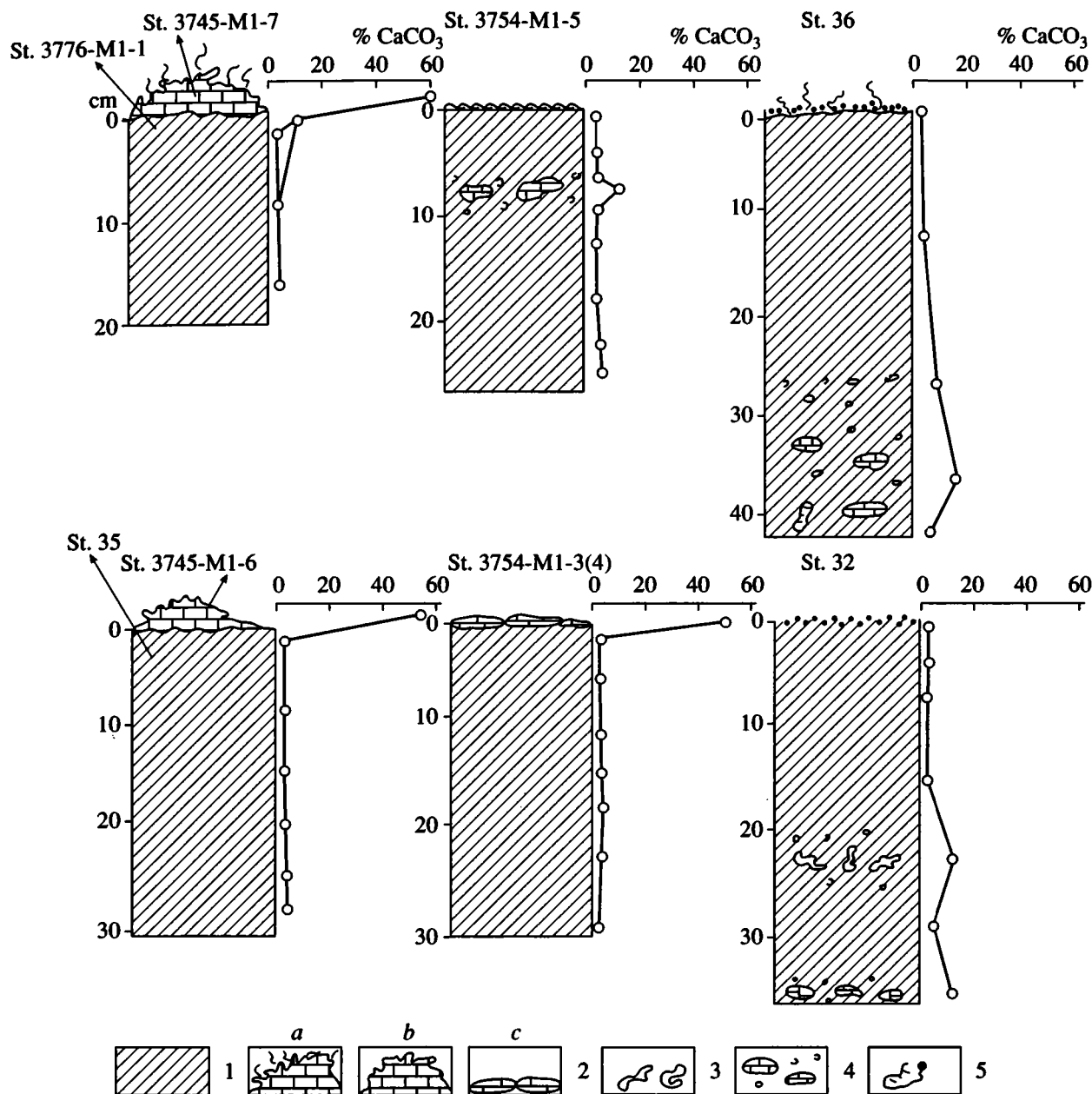
The chemical composition of interstitial water, after its pressing out by pneumatic press, was analyzed on board the research vessel (Shishkina, 1972). A biotronic ion chromatograph (Germany) was applied to determine sulfate the ion content.

Rates of biogeochemical processes were measured by radioisotope methods directly in the shipboard laboratory. Appropriate <sup>35</sup>S and <sup>14</sup>C compounds served as substrates (Pimenov *et al.*, 1997).

## RESULTS

### *Morphology of Authigenic Carbonates and Their Position in Sedimentary Sections*

Authigenic carbonate bodies from the HMMV caldera are variable in their morphology (Figs. 3, 4, 5). They comprise coral-shaped buildups, up to 30 cm



**Fig. 5.** Morphology of authigenic carbonate bodies and their position in the sediment section. (1) Dark gray to black, nonstratified,  $\text{CH}_4$ -bearing, reduced sediments; morphology of bodies: (2) builds up on the bottom surface, from several centimeters to 30 cm high: (a) coral-shaped living builds up with *Pogonophora* on the surface, (b) coral-shaped builds up, (c) plate-like bodies; carbonate builds up in sedimentary cover: (3) dark gray irregular bodies; (4) light-colored flat "pebbles" with numerous molds of sponge spicules; (5) fragment of carbonate chimney with hollow channels inside (length ~17 cm). Sizes of carbonate bodies vary from several millimeters to 17 cm. The carbonate content is determined using volumetric method.

high, and carbonate cement of surface sediments ("plates") occurring on the bottom surface (Fig. 5), as well as carbonate crusts, buildup fragments, "tubes" with numerous channels, some of which are hollow, and rounded flat carbonate clasts ("pebbles") buried within sediments.

Authigenic carbonate builds up on the bottom surface (Figs. 2, 3) are subdivided into "living" and

"extinct" ones. The living builds up occur in the most active central part of the caldera (Station 3745-M1-7), and are overgrown with benthic fauna. Their base is buried in black reduced sediments, which contain methane and free hydrogen sulfide. Samples of "extinct" builds up were collected from the hilly zone at the caldera periphery among oxidized sediments, where  $\text{CH}_4$ -bearing fluids are not venting onto the bottom today (stations 3745-M1-6 and 3754-M1-3).

**Table 1.** Chemical composition of carbonate bodies from the HMMV caldera (results of X-ray fluorescence analysis, %)

| Station no. | Morphology                                      | CaCO <sub>3</sub> | C <sub>org</sub> | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | TiO <sub>2</sub> | Fe <sub>2</sub> O <sub>3</sub> | CaO  | MnO   | MgO  | Na <sub>2</sub> O | K <sub>2</sub> O | I.O.I. | Σ        |
|-------------|-------------------------------------------------|-------------------|------------------|------------------|--------------------------------|------------------|--------------------------------|------|-------|------|-------------------|------------------|--------|----------|
| 3745-M1-7   | Coral-shaped carbonate buildup, 40 × 20 × 15 cm | 47                | 0.31             | 25.42            | 7.34                           | 0.53             | 2.73                           | 28.3 | 0.077 | 2.65 | 2.50              | 1.60             | 27.62  | 100.70*  |
| 3754-M1-3   | Carbonate buildup (fragment)                    | 41                | 0.34             | 29.68            | 8.01                           | 0.69             | 2.35                           | 25.4 | 0.036 | 2.84 | 2.50              | 1.34             | 26.28  | 99.12*   |
| 32/20–30 cm | Irregular bodies (2–4 cm)                       | 37                | 0.36             | 37.61            | 7.28                           | 0.43             | 2.65                           | 22.8 | 0.050 | 2.91 | 0.97              | 1.56             | 23.50  | 99.76**  |
| 32/45–55 cm | Flat nodules with smooth surface                | 44                | 0.45             | 29.84            | 6.37                           | 0.39             | 2.80                           | 27.3 | 0.086 | 3.62 | 0.99              | 1.53             | 27.00  | 99.93**  |
| 36/30–45 cm | Flat nodules with smooth surface (2–4 cm)       | 50                | 0.32             | 27.95            | 5.36                           | 0.34             | 2.33                           | 30.3 | 0.096 | 3.06 | 0.87              | 1.44             | 28.30  | 100.05** |
| 36/40–45 cm | Fragment of hollow tube ("chimney")             | 40                | 0.37             | 36.20            | 7.16                           | 0.40             | 2.72                           | 24.5 | 0.063 | 2.34 | 1.14              | 1.65             | 23.90  | 100.07** |

\* Analyst T.G. Kuzmina; Institute of Oceanology, Russian Academy of Sciences; \*\* analyst I.A. Roshchina, Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences.

Sediments enclosing authigenic carbonates can be subdivided into strongly reduced ones with high CH<sub>4</sub> content (Station 3754-M1-5) and low (less than 5 ml/l) CH<sub>4</sub> content (stations 32, 36). In the latter, CH<sub>4</sub>-gas hydrates were found within sediments at 80 cm below the seafloor (Station 32), and carbonates occur in the sediment layer 20–45 cm.

Carbonate "pebbles" are represented by light gray, slightly lithified and easily friable bodies with numerous small holes at their surface, in some cases filled by thin siliceous sponge spicules. "Pebbles" are likely rounded fragments of carbonate plates formed on the sediment surface during an early stage of carbonate precipitation, when sediments were cemented by carbonate at sites of CH<sub>4</sub>-bearing fluid discharge. Sponges preferred to inhabit such still nonlithified but somewhat harder substrate as compared with surrounding mud, and their molds are observed at the surface of "pebbles."

Irregular carbonate bodies, up to 5 cm in size (Station 32, interval 20–30 cm), resemble fragments of an upper part of coral-shaped carbonate buildups, which consist of numerous *Pogonophora* tubes and sponge spicules cemented by carbonate. Most of such fragments have smooth rounded surfaces (Fig. 4), unlike rough surfaces of the coral-shaped buildups (Fig. 3). This is evidence of their replacement.

Another type of carbonate bodies occurring within sediments is represented by a "chimney" fragment with a system of hollow channels inside. The length of the "chimney" fragment, is 17 cm along the axis of main channel. Such a "chimney" can grow on the seafloor as a result of ascending methane migration and its oxidation that led to carbonate cementation of sediments around the channel.

Morphology of the authigenic carbonate bodies indicates that they are not formed within sediments *in situ*, but instead, at the bottom–water interface, in conditions of diffuse or bubble CH<sub>4</sub>-bearing fluid discharge.

### *Composition and Structure of Authigenic Carbonate Bodies*

The **chemical composition** (Table 1) was determined in specimens of morphologically similar carbonate bodies selected from certain sediment layers and buildups. Along with carbonates, samples contain silica and components of aluminosilicate (clay) minerals. The silica content in the sample of "chimney" fragment and in samples of irregular bodies is by 6–9% higher than that in other samples. Carbonate (CaCO<sub>3</sub>) content in analyzed samples varies from 37 to 50%, according to X-ray fluorescence data, and from 47 to 68% as determined by volumetric method. C<sub>org</sub> content is more than 0.5% (Table 1). When calculated on the carbonate-free basis, the chemical composition of an authigenic sample is similar to that of CH<sub>4</sub>-bearing caldera sediments (Lein *et al.*, 1998).

The study of thin sections of the authigenic carbonates showed that they consist of terrigenous clastic inequigranular minerals enclosed in pelitomorph clay–carbonate cement (Fig. 6). Clastic terrigenous material content varies from 40 to 60%. The clastic component includes quartz (about 25%), feldspars (about 10%), and chlorite and biotite (2–5%). Organic remains (up to 5%) comprise fragments of *Pogonophora* tubes, sponge spicules, foraminiferal tests, and rare gastropods and shell fragments (Fig. 6). Diagenetic minerals are represented by thin zeolite veinlets and pyrite framboids.

**Structures of carbonate bodies.** The thin section study of different parts of buildups, from the base to the top, showed that a dense massive structure of the pelitomorph clay–carbonate cement prevails at their contact with sediments. This structure gradually changes upward, being replaced by porous biogenic structure (Fig. 6). Massive structure is also characteristic for "pebbles." A porous biogenic structure dominates in fragments of irregular shape, which are possibly broken off the buildups tops.

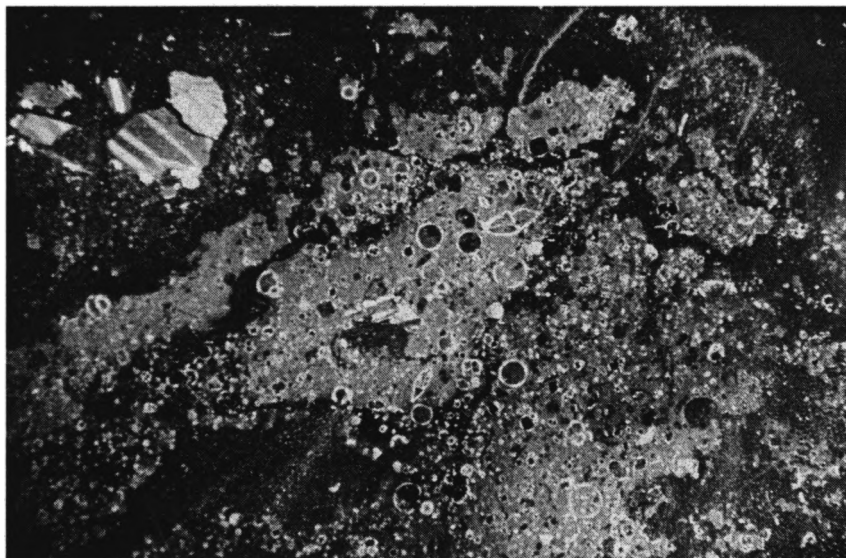


Fig. 6. Characteristic microstructure of authigenic carbonates (thin section, magn. 300, St. 3745-M1-7). The porous rock consists of clastic terrigenous material (quartz and feldspar grains) and biogenic remains (sponge spicules, foraminiferal tests, shell fragments) cemented by pelitic matrix of clay-carbonate matrix.

### Mineralogy of Authigenic Carbonates

It is shown that calcite represented by aggregates of micrometer-size particles is the main mineral phase in authigenic carbonates (Figs. 7a, 8a, 8b, 9a, 9c). Characteristic peaks of Ca and O are observed in energy-dispersive spectra (Fig. 7b). Magnesium, a common component of marine authigenic carbonates (Lein *et al.*, 1989; Suess *et al.*, 1998; Von Rad *et al.*, 1996), is not found in any of the energy-dispersive spectra obtained. X-ray diffraction confirmed that calcite is the only carbonate mineral in studied samples.

Rare particles and aggregates of Sr-bearing barite are fixed in carbonate cement (Figs. 7b, 8a, 8b, 9c). The obtained barite spectra (Fig. 8c) contain characteristic peaks of Ba, S, O, and Sr. Strontium replaces isomorphically Ba in the barite lattice. Approximate crystallochemical formulas of calcite [ $\text{Ca}_{0.85}\text{C}_{1.2}\text{O}_{3.23}$ ] and barite [ $(\text{Ba}_{0.99}\text{Sr}_{0.04})_{1.03}\text{S}_{0.94}\text{O}_{3.86}$ ] are calculated. The calcite cement encloses potassium phyllosilicates (Figs. 9a–9c), with Si, Al, K, Mg, and Fe peaks in their spectra. This mineral is close to illite in its composition. Based on a X-ray diffraction analysis of less than 0.001 mm fraction, we noted earlier that illite predominates among clay minerals detected in authigenic carbonates from stations 32 and 36 (Lein *et al.*, 1998).

Angular quartz grains (Figs. 7c, 8b, 9a) and hollow conical opal tubes (sponge spicules), from 10 to 2000  $\mu\text{m}$  long (Figs. 7a, 8a, 9b) were found besides the terrigenous material within the calcite cement. Spicules are especially abundant in microscopic hollows of the carbonate buildup from Station 3745-M1-7, where the diameter of the hollows is 3–4 mm (Fig. 9c).

An absence of magnesian carbonates and aragonite among the authigenic carbonates is, perhaps, the most

interesting and unexpected result of the mineralogical study.

### Isotopic Composition of Carbon and Oxygen in Authigenic and Dispersed Carbonates

The carbonate content in  $\text{CH}_4$ -bearing sediments from the HMMV caldera varies from 2.2 to 4.6%. The  $\delta^{13}\text{C}$  values in this dispersed carbonate ranges from  $-3.6\text{‰}$  to  $-8.3\text{‰}$ , and average of 10 measurements is  $-5.8\text{‰}$  (Table 2).

Heavier carbon isotopic composition ( $\delta^{13}\text{C}_{\text{av}} = -1.9\text{‰}$ ), close to that of normal marine carbonates, is characteristic for dispersed carbonate from Holocene hemipelagic sediments of the HMMV caldera (Lein *et al.*, 1998).

The  $\delta^{13}\text{C}$  values in all morphological types of authigenic carbonates vary within narrow limits, from  $-28.4\text{‰}$  to  $-29.6\text{‰}$  (Table 2). The only exception is the "chimney" fragment, where a heavier carbon isotopic composition ( $\delta^{13}\text{C} = -16.6\text{‰}$ ) is measured (Table 2). A microscopic study showed that this fragment contains more than 10% of shell carbonate with isotopically heavier carbon.

Negative values of oxygen isotopic composition, with  $\delta^{18}\text{O}$  ranging from  $-5.1\text{‰}$  to  $-9.8\text{‰}$ , are measured in dispersed carbonate (Table 2). The  $\delta^{18}\text{O}$  of authigenic carbonates is within positive values and shows minor variations from  $4.3\text{‰}$  to  $5.4\text{‰}$  (Table 2). Moreover, it should be noted that the oxygen isotopic composition of authigenic carbonates is heavier, as compared with that of bottom water, interstitial water, and water of  $\text{CH}_4$ -gas hydrates (Table 3). We have to search for an explanation of such a heavy oxygen isotopic

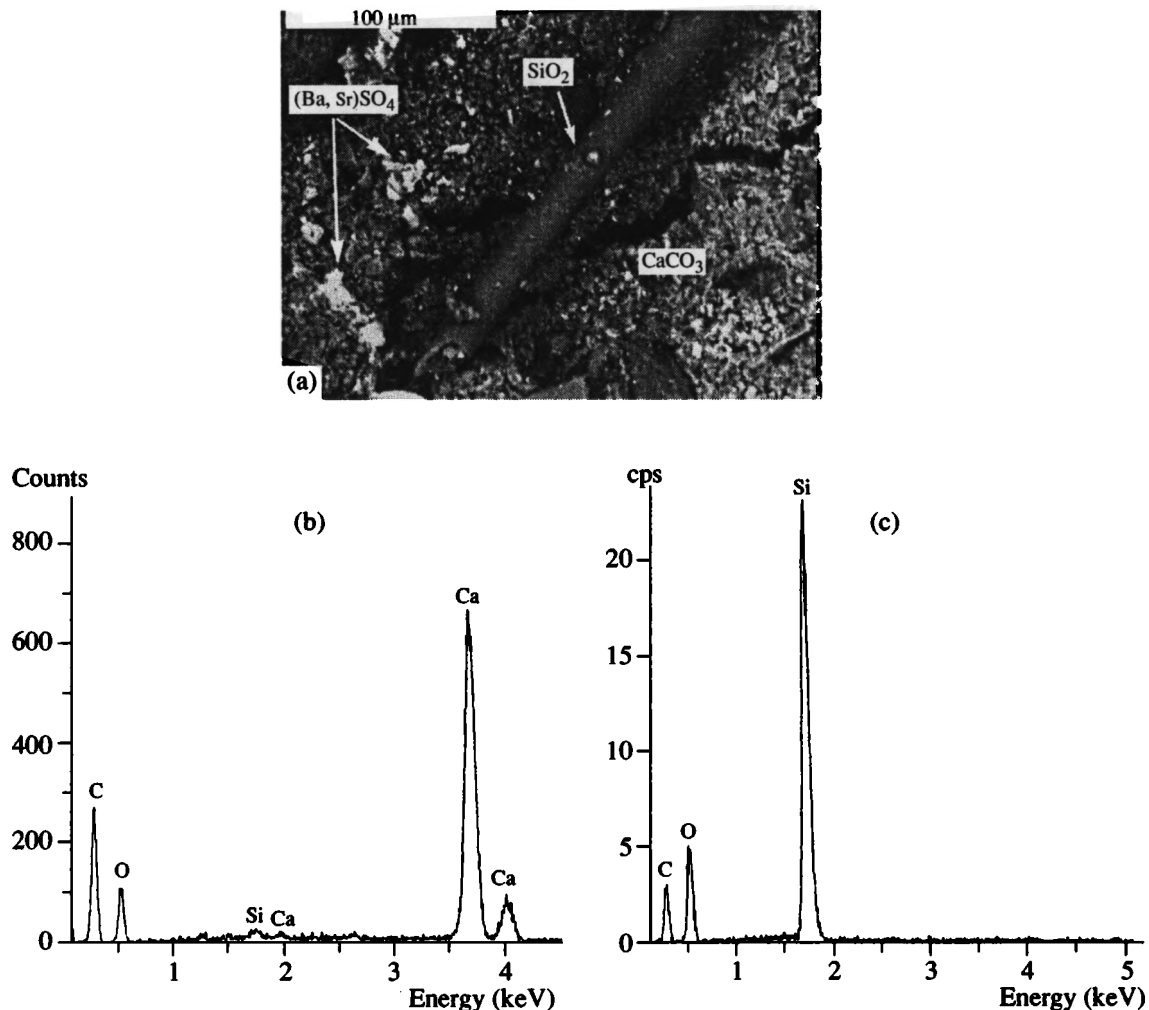


Fig. 7. (a) (SEM) image of the carbonate buildup from St. 3754-M1-3 and energy-dispersive spectra of its major constituents: (b) carbonate and (c) silica. Carbon peak is a reflection of artificial carbon powder film. Analyst A.I. Gorshkov, IGEM.

composition of authigenic carbonates in their formation mechanisms.

#### *Radiocarbon Age of a Carbonate Buildup*

Five samples of the living buildup from Station 3745-M1-7 were analyzed for radiocarbon dating (Table 4). The radiocarbon age varies from  $7960 \pm 410$  to  $11\,380 \pm 530$  yr BP in samples from different parts of the buildup.

The following carbon sources contribute to the formation of the buildup: (1) carbon of CO<sub>2</sub> formed during CH<sub>4</sub> oxidation; (2) carbon of HCO<sub>3</sub><sup>-</sup> ion in interstitial water of sediments, where active organic matter destruction takes place; (3) bicarbonate of the bottom water; and (4) sedimentary (planktonic) carbonate, as a mechanical admixture. The radiocarbon age of the buildup may change depending on a relative contribution of different carbon sources listed. The youngest

age was obtained for coral-shaped carbonate overgrowths at the buildup top (Table 4).

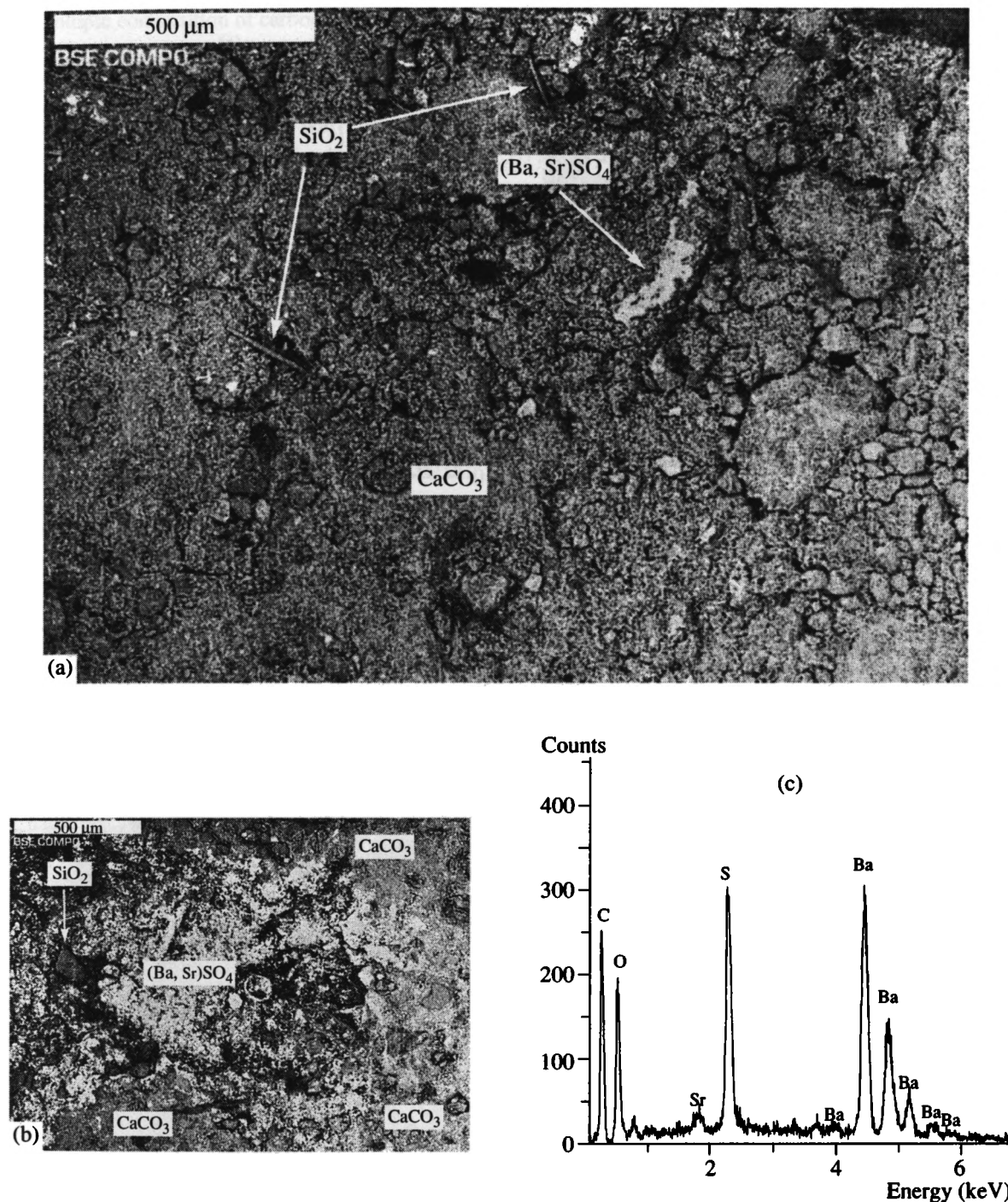
#### DISCUSSION

Authigenic carbonates are widespread in sediments of internal (Black Sea, Baltic Sea) and marginal seas (Sea of Okhotsk, North Sea, Bering Sea), as well as in gulfs and bays (Gulf of Mexico, Bay of California, Persian Gulf) of both active and passive continental margins (Aharon *et al.*, 1997; Carson *et al.*, 1994; Lein *et al.*, 1979; Le Pichon *et al.*, 1990; Suess *et al.*, 1998; Von Rad *et al.*, 1996).

Occurrences of authigenic carbonates are not always related to active methane seep fields, such as HMMV, where about 100 000 m<sup>3</sup> of CH<sub>4</sub> is oxidized each year (Lein *et al.*, 2000).

All main features of cold methane seeps are observed in the HMMV caldera. Among those, the following ones are especially important to understand the

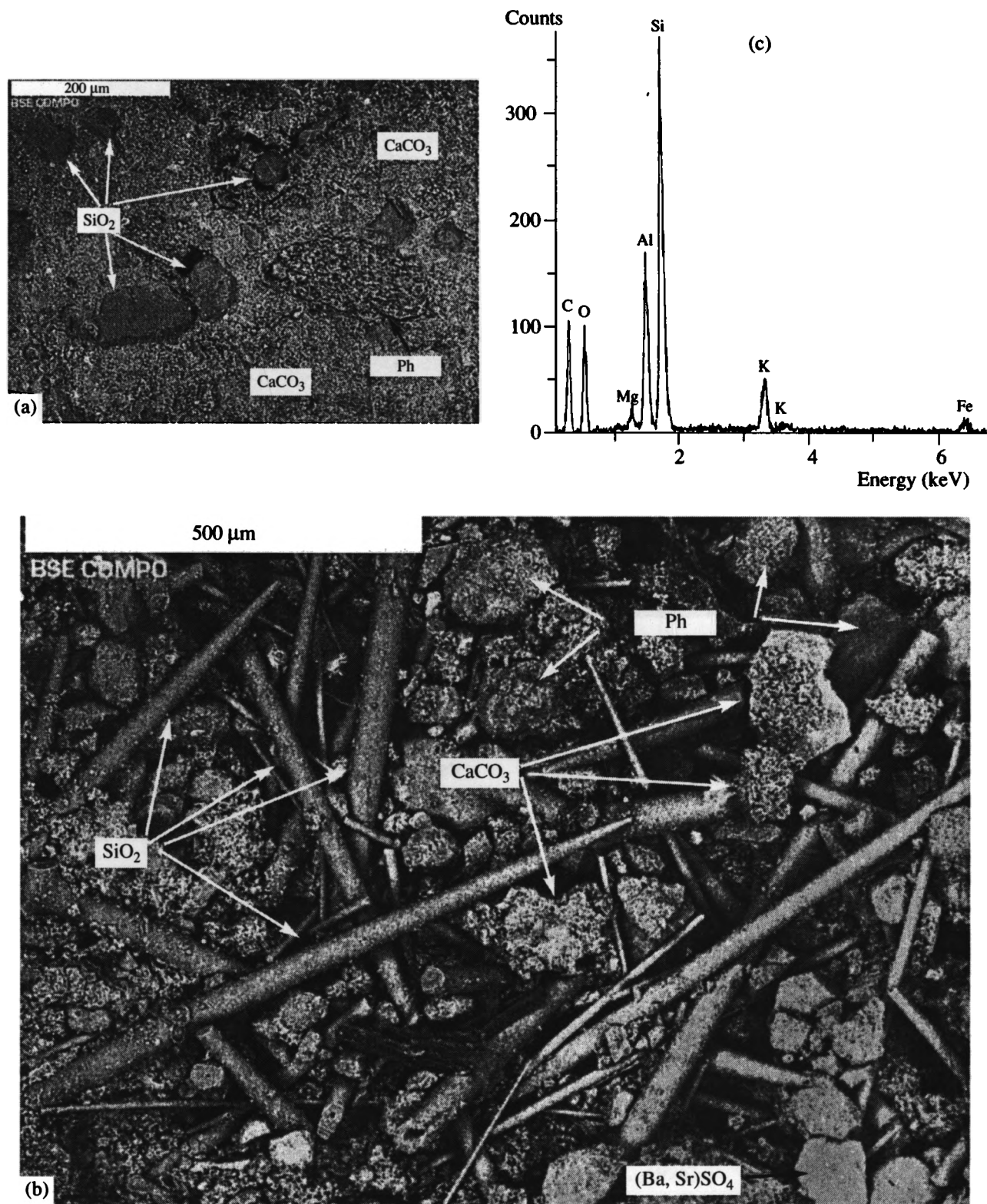




**Fig. 8.** (a, b) SEM images of two authigenic carbonate samples from St. 3754-M1-5; and (c) energy-dispersive spectrum of Sr-barite. Carbon peak is a reflection of artificial carbon powder film. Analyst A.I. Gorshkov, IGEM.

authigenic carbonate formation: (1) anomalous composition of interstitial waters in surface sediments, which represent an admixture of CH<sub>4</sub>-bearing fluid, diagenetic interstitial water, and bottom seawater (Table 5); (2) high rates of anaerobic bacterial methane oxidation and sulfate reduction (Fig. 10); and (3) authigenic carbonate formation. Figure 10 shows that

processes of anaerobic CH<sub>4</sub> oxidation and sulfate reduction are intense at sites with authigenic carbonates within the caldera (stations 3745-M1-3 and 3754-M1-5). Authigenic carbonates are not forming in areas where anaerobic microbial methane oxidation and sulfate reduction processes are negligible (stations 36 and 37).



**Fig. 9.** SEM images of a carbonate buildup sample from St. 3745-M1-7 and energy-dispersive spectrum of a phyllosilicate (Ph). (a) Lower part of the buildup at the contact with underlying mud; dense massive material contains quartz grains and phyllosilicate flakes in the pelitomorphous clay-carbonate cement; (b) porous material from the top of living buildup that consists of siliceous sponge spicules and terrigenous particles, cemented by authigenic carbonate and Sr-barite; (c) energy-dispersive spectrum of phyllosilicate flake. Carbon peak is a reflection of artificial carbon powder film. Analyst A.I. Gorshkov, IGEM RAS.

**Table 2.** Isotopic composition of carbon and oxygen in dispersed and authigenic carbonates

| Station no.                                                              | Interval, cm | Sample description                                                                      | $\delta^{13}\text{C}$ , ‰<br>PDB | $\delta^{18}\text{O}$ , ‰<br>PDB | $\delta^{13}\text{C-C}_{\text{org}}$ , ‰<br>PDB |
|--------------------------------------------------------------------------|--------------|-----------------------------------------------------------------------------------------|----------------------------------|----------------------------------|-------------------------------------------------|
| Dispersed carbonates from sediments with $\text{CH}_4$ content > 50 ml/l |              |                                                                                         |                                  |                                  |                                                 |
| 3754-M1-5**                                                              | 0–2          | Reduced sediments with high $\text{CH}_4$ and $\text{H}_2\text{S}$ contents             | –4.3                             | –                                | –25.7                                           |
|                                                                          | 15–20        |                                                                                         | –7.2                             | –                                | –25.3                                           |
| 3776-M1-1*                                                               | 0–15         | $\text{CH}_4$ -bearing sediments ( $\text{CH}_4 \geq 300$ ml/l), with free hydrocarbons | –8.3                             | –                                | –25.4                                           |
| 3745-M1-5**                                                              | 0–7          |                                                                                         | –7.2                             | –                                | –23.8                                           |
| 30***                                                                    | 0–20         |                                                                                         | –5.3                             | –9.8                             | –25.1                                           |
| 31***                                                                    | 40–90        |                                                                                         | –5.1                             | –8.9                             | –                                               |
| 45***                                                                    | 0–10         | Sediments containing $\text{CH}_4$ -gas hydrate                                         | –4.1                             | –5.4                             | –25.8                                           |
| 45***                                                                    | 190–200      |                                                                                         | –3.6                             | –5.5                             | –26.3                                           |
| Dispersed carbonates from sediments with $\text{CH}_4$ content < 50 ml/l |              |                                                                                         |                                  |                                  |                                                 |
| 32***                                                                    | 0–20         | Reduced sediments with low $\text{CH}_4$ content                                        | –7.0                             | –                                | –                                               |
| 36***                                                                    | 5–10         |                                                                                         | –6.0                             | –5.1                             | –                                               |
| Authigenic carbonates                                                    |              |                                                                                         |                                  |                                  |                                                 |
| 3745-M1-7*                                                               | Buildups     | Living buildup with <i>Pogonophora</i> on its surface                                   | –28.4                            | 4.9                              | –32.8                                           |
| 3754-M1-5*                                                               | 5–10         | Irregular crusts                                                                        | –28.5                            | 5.4                              | –53.0                                           |
| 3758**                                                                   | 60–70        | Smooth “pebbles”                                                                        | –29.5                            | –                                | –25.7                                           |
| 32***                                                                    | 20–30        | Irregular crusts                                                                        | –28.7                            | 5.1                              | –30.7                                           |
|                                                                          | 45–55        | Smooth “pebbles”                                                                        | –28.4                            | 4.9                              | –30.5                                           |
| 36***                                                                    | 30–40        | Smooth “pebbles”                                                                        | –29.6                            | 4.3                              | –30.2                                           |
|                                                                          | 40–42        | Chimney fragment                                                                        | –16.6                            | 5.0                              | –30.1                                           |

\* Analyst V.S. Lebedev, All-Russian Institute of Mineral Resources; \*\*analyst Yu.M. Miller, Institute of Microbiology, Russian Academy of Sciences; \*\*\* data from (Lein *et al.*, 1998).

**Table 3.** Isotopic composition of oxygen and hydrogen in seawater, interstitial water, and gas hydrate

| Station no. | Sampling interval | Sample description                                                                               | $\delta^{18}\text{O}$ , ‰ PDB | $\delta\text{D}$ , ‰ |
|-------------|-------------------|--------------------------------------------------------------------------------------------------|-------------------------------|----------------------|
| 3745-M1-1   | Near-bottom       | Seawater beyond the caldera                                                                      | 0.30                          | 1.0                  |
| 3776-M1-1   | Near-bottom       | Seawater from the central zone of the caldera                                                    | –0.15                         | –6.0                 |
| 45          | 0–5 cm            | Interstitial water from sediment layer with gas hydrate                                          | 0.20                          | –5.0                 |
| 45          | 215–220 cm        | Interstitial water from sediment layer with gas hydrate; possible admixture of gas hydrate water | –1.3                          | –19.0                |
| 32          | 40–50 cm          | Interstitial water from sediments with low $\text{CH}_4$ content                                 | 1.14                          | –20.0                |
| 32          | 70–85 cm          | Gas hydrate water                                                                                | 2.62                          | –6.0                 |

Analyst B.G. Pokrovskii (Institute of Geology, Russian Academy of Sciences).

Studied authigenic carbonate bodies of different morphologies have similar chemical compositions (Table 1) and isopic compositions of carbon and oxygen in carbonates (Table 2). They consist of clastic terrigenous material cemented by calcite and Sr-barite (Figs. 6–8).

The morphology and structure of carbonate buildups, as well as the similarity between buildups and morphologically variable bodies in sediments, suggest that the latter are destruction products of authigenic carbonates formed at the water–bottom interface. Car-

bonate fragments might be transported from sites of their primary formation by mud flows to be finally buried in deposits of these flows. We registered at least three episodes of intense mud volcano activity in a core section of mud from the southern part of the caldera (Station 3774). Therefore, carbonate bodies in sediments occur not *in situ*, but instead, they represent a clastic material reworked from the bottom surface and buried in mud flow deposits.

The carbon isotopic composition of authigenic carbonates is depleted in heavy isotope  $\delta^{13}\text{C}$ , as it is typi-

**Table 4.** Radiocarbon age of the authigenic carbonate buildup from St. 3745-M1-7

| Sample no. | Sampling location                                                               | <sup>14</sup> C age, yr |
|------------|---------------------------------------------------------------------------------|-------------------------|
| 1          | Porous top of the carbonate buildup with abundant <i>Pogonophora</i> tubes      | 8680 ± 160              |
| 2.1        | Massive "plate" at the buildup base                                             | 11380 ± 530             |
| 2.2        | Coral-shaped buildup surface                                                    | 10730 ± 240             |
| 3          | Coral-shaped surface from the central part of the buildup (close to Sample 2.2) | 10750 ± 620             |
| 4          | Coral-shaped outgrowths at the porous buildup top with <i>Pogonophora</i> tubes | 7960 ± 410              |

Note: "Trench" sampling was performed from the massive buildup base buried in dark gray mud with hydrogen sulfide (2.1) to the porous lateral surface (2.2) of the buildup; analyst V.M. Kuptsov (Institute of Oceanology, Russian Academy of Sciences).

**Table 5.** Average chemical and isotopic compositions of interstitial water from the HMMV caldera sediments (Lein *et al.*, 1998, with additions)

| Interstitial water                                       | Chemical composition |                               |                 |                  |                  |                              |       | Isotopic composition, ‰                         |                     |                                   |                    |                                                 |
|----------------------------------------------------------|----------------------|-------------------------------|-----------------|------------------|------------------|------------------------------|-------|-------------------------------------------------|---------------------|-----------------------------------|--------------------|-------------------------------------------------|
|                                                          | Cl <sup>-</sup>      | SO <sub>4</sub> <sup>2-</sup> | Br <sup>-</sup> | Ca <sup>2+</sup> | Mg <sup>2+</sup> | NH <sub>4</sub> <sup>+</sup> | Alk   | δ <sup>13</sup> C-HCO <sub>3</sub> <sup>-</sup> | δD-H <sub>2</sub> O | δ <sup>13</sup> C-CH <sub>4</sub> | δD-CH <sub>4</sub> | δ <sup>34</sup> S-SO <sub>4</sub> <sup>2-</sup> |
| Gas-saturated, St. 30 and 31                             | 359                  | 1.1                           | 2711            | 14.0             | 72.0             | 42.5                         | 27.9  | —                                               | —                   | -56.6                             | —                  | —                                               |
| Gas hydrate, St. 45                                      | 294                  | 1.0                           | 2860            | 10.0             | 18.0             | 48.3                         | 19.5  | 2.3                                             | -16.0               | -61.0                             | -242.0             | —                                               |
| Hemipelagic sediments, St. 22 and 23                     | 500                  | 19.5                          | 890             | 36.0             | 18.7             | 2.1                          | 7.7   | -20.0                                           | -1.7                | —                                 | —                  | 19.6                                            |
| Bottom seawater, St. 3776-M1-1                           | 538                  | 28.7                          | —               | 10.36            | 55.31            | n.d.                         | 2.43  | —                                               | -0.15               | —                                 | —                  | 19.2                                            |
| Surface sediments at the site of living buildup, 0–10 cm | 385                  | 0.86                          | —               | 1.47             | 7.24             | 3.03                         | 22.75 | —                                               | -6.0                | —                                 | —                  | 30.0                                            |

Note: Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> are given in mmol; Br<sup>-</sup> and NH<sub>4</sub><sup>+</sup> are given in μmol; (—) no data; (n.d.) not detected.

cal for carbon dioxide formed during microbial methane oxidation (Table 2). Observed δ<sup>13</sup>C variations in authigenic carbonates are explained, first, by a difference in isotopic composition of CH<sub>4</sub> from different sources, and second, by a presence of isotopically heavy marine carbonate (shell fragments) in the carbonate bodies.

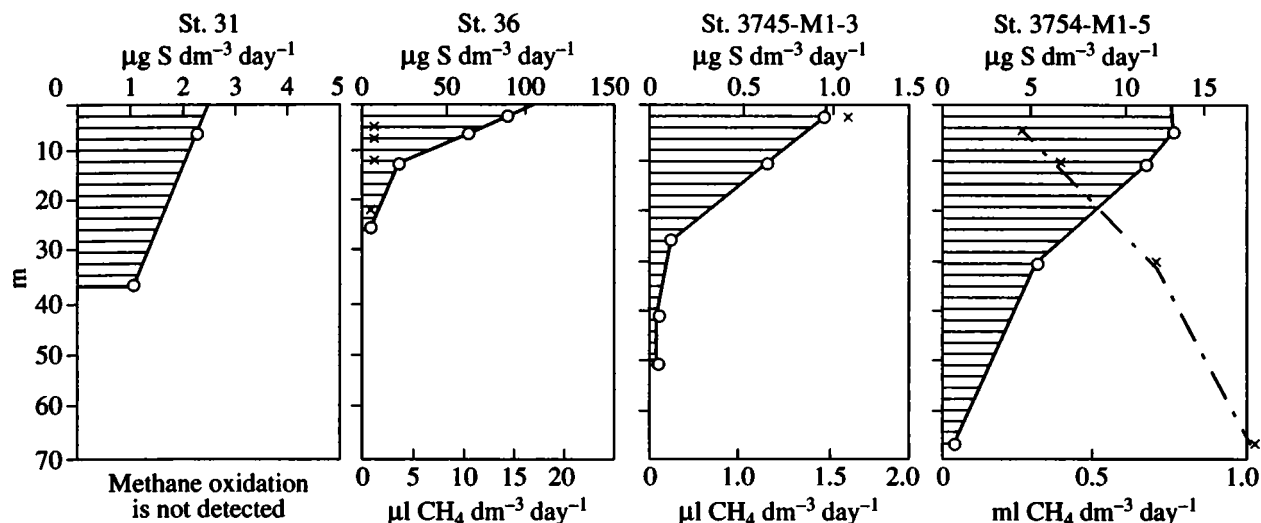
The oxygen isotopic composition of authigenic carbonates, on the contrary, is very uniform and heavy, differing from the isotopic composition of all compounds present in the reaction zone (Tables 3, 4). Heavy oxygen isotopic composition is a characteristic feature of most known authigenic carbonates formed with a contribution of CH<sub>4</sub> carbon (Lein *et al.*, 1989; Suess *et al.*, 1998; Von Rad *et al.*, 1996).

The anomalous isotopic composition of carbon and oxygen in authigenic carbonates is commonly explained in terms of CH<sub>4</sub> oxidation by sulfate ion of the seawater according to reaction: CH<sub>4</sub> + SO<sub>4</sub><sup>2-</sup> → HCO<sub>3</sub><sup>-</sup> + HS<sup>-</sup> + H<sub>2</sub>O. It is assumed that this reaction leads to an input into carbonate of isotopically light carbon from CH<sub>4</sub> and of isotopically heavy oxygen from sulfate ion (Alperin *et al.*, 1992; Esikov and Pashina,

1990; Reeburg, 1980; Reeburg and Alperin, 1988). However, this reaction is energetically disadvantageous for sulfate reducing bacteria, and, thus, seems improbable (Ivanov, 1964).

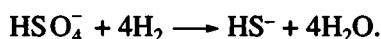
Certain geochemical evidence prove that methane in the caldera sediments is oxidized under anaerobic conditions (Lein *et al.*, 1998). Pure cultures of anaerobic methanotrophs have not been detected, but it is known that methane producers can oxidate methane in conditions of excess methane within the reaction zone to produce carbon dioxide and hydrogen (Zehnder and Brock, 1979). Our studies revealed a migrational nature of CH<sub>4</sub> (Lein *et al.*, 1998), and showed that the modern process of methane formation practically does not work in the caldera sediments (Pimenov *et al.*, 1997).

Hydrogen sulfide is also commonly present in marine anaerobic ecosystems with high methane content, including the HMMV caldera sediments. The highest rates of bacterial sulfate reduction are observed in surface sediments from HMMV (Fig. 10). Microbiological studies allow us to suggest that a microbial community composed of methane producers and sulfate reducers participates in the process of anaerobic methane oxidation. Methane producers oxidate CH<sub>4</sub>



**Fig. 10.** Distribution diagram of (1) sulfate reduction rate and (2) anaerobic methane oxidation rate in a typical sediment section from the HMMV caldera. Samples were obtained by gravity corer (St. 31), box corer (St. 36), and the sediment sampler of *Mir-1* submersible (St. 3745-M1-3 and 3754-M1-5). In gas-saturated sediments from St. 31, the residual  $\text{CH}_4$  concentration is 100–300 ml/l, methane oxidation is not observed, and the sulfate reduction rate is low. In sediments from St. 36 with a low  $\text{CH}_4$  content ( $\leq 1\text{--}3$  ml/l), the anaerobic methane oxidation rate is  $0.09\text{--}0.64 \text{ CH}_4/\text{dm}^3 \text{ day}^{-1}$ , and the sulfate reduction rate rises up to  $100 \mu\text{g S dm}^{-3} \text{ day}^{-1}$ . In sediments from St. 3745-M1-3, and especially from St. 3754-M1-5, the rates of microbiological sulfate reduction and methane oxidation are very high ( $1\text{--}15 \text{ mg S dm}^{-3} \text{ day}^{-1}$  and  $1.1\text{--}1.57 \text{ ml CH}_4 \text{ dm}^{-3} \text{ day}^{-1}$ , respectively).

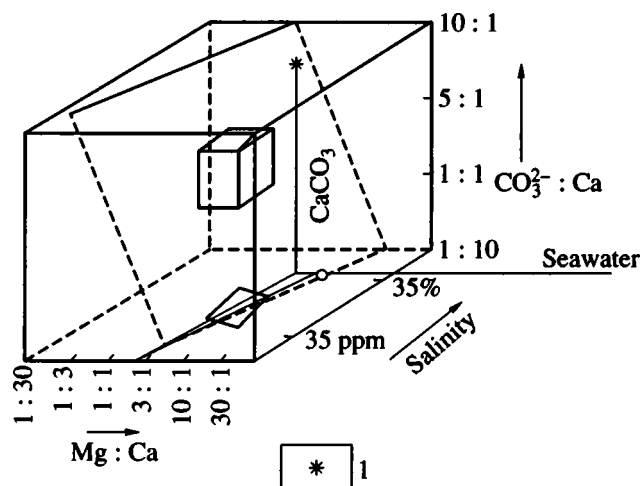
with the formation of  $\text{H}_2$  (Hoebler *et al.*, 1994). Hydrogen serves as a perfect substrate for the development of sulfate reducers according to the reaction:



Geochemical activity of such bacterial community leads to the production of  $\text{CO}_2$  (83%) and  $\text{C}_{\text{org}}$  (biomass of bacteria and their exometabolites), as well as hydrogen sulfide and its products (Lein *et al.*, 2000). Authigenic carbonates cannot form within sediments owing to a rapid exhausting of sulfate ion, the necessary substrate for the bacterial community development. The heavy isotopic composition of carbonates, drastically differing from that of the bottom water and interstitial water oxygen, as well as from that of  $\text{HCO}_3^-$  ion in interstitial water (Tables 2, 3), confirms a contribution of the isotopically heavy seawater sulfate oxygen into the authigenic carbonate formation that takes place due to activity of the methane-oxidizing and sulfate-reducing bacterial community.

The formation of carbon dioxide in the process of methane oxidation leads to an increase in total  $\Sigma\text{CO}_3^{2-}$  in the interstitial water of surface sediments. In other words, only microbiological processes create physico-chemical conditions necessary for the carbonate precipitation. For example, the concentration of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in the interstitial water of the uppermost sediment layer (0–10 cm) from the area of the living buildup is 10 times lower than that in interstitial water of surrounding sediments and in the bottom water (Table 5).

If interstitial water becomes oversaturated with carbon dioxide,  $\text{Ca}^{2+}$  ions will be extracted from the water to form carbonate. Ion ratios in interstitial water are  $\text{Mg}^{2+} : \text{Ca}^{2+} = 3.3 : 1$ ;  $\Sigma\text{CO}_3^{2-} (\text{Alk}) : \text{Ca}^{2+} = 5.7 : 1$ . In the diagram (Fig. 11), these parameters characterize the field of calcium carbonate precipitation without  $\text{Mg}^{2+}$ .



**Fig. 11.** Diagram showing the influence of three factors (salinity,  $\text{Mg} : \text{Ca}$  ratio, and  $\text{CO}_3^{2-} : \text{Ca}$  ratio) in solution on calcium carbonate and dolomite precipitation (Nechiporenko and Bondarenko, 1988). (1) Crystallization point of pure calcite from interstitial water of sediments at St. 3776-M1-1 (interval 0–10 cm) near the authigenic carbonate buildup at St. 3745-M1-7 (Fig. 1; Table 5).

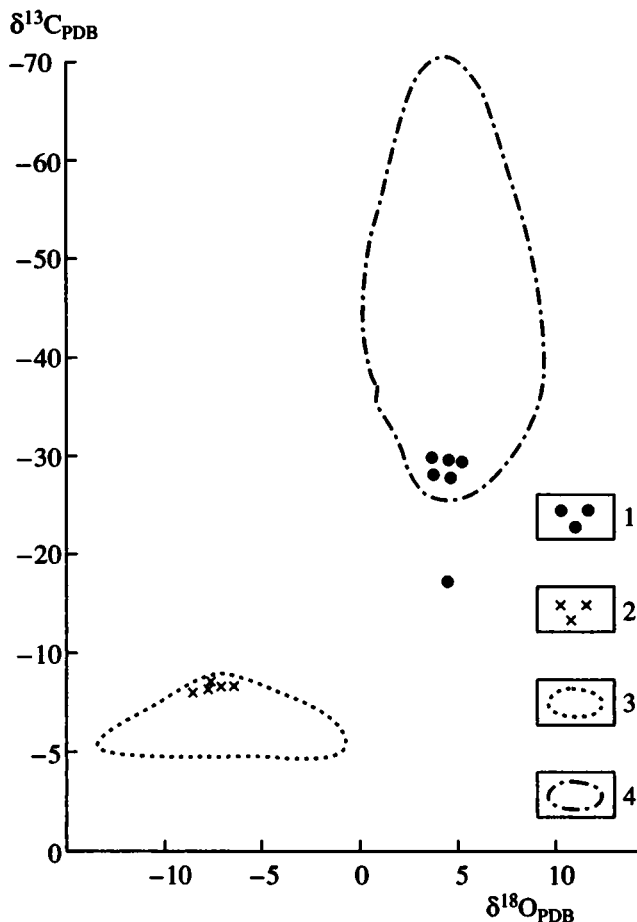


Fig. 12. Isotopic composition of carbon and oxygen in (1) dispersed and (2) authigenic carbonates from the HMMV caldera. Field boundaries of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values characteristic for (3) dispersed carbonates in hemipelagic sediments and (4) authigenic carbonates. All isotope data are normalized to the PDB value.

admixture. Therefore, physicochemical conditions of carbonate precipitation and composition of carbonates ( $\text{CaCO}_3$ ) in the living buildup show a good correspondence.

Crystallization of carbonate as calcite takes place in conditions of negative temperature on the caldera bottom ( $T = -1^\circ\text{C}$  in July and August). Crystallization of aragonite and high-Mg calcite requires positive temperatures (Lazarenko, 1971; Von Rad *et al.*, 1996).

In the  $\delta^{13}\text{C}$  versus  $\delta^{18}\text{O}$  diagram for marine carbonates (Fig. 12), dispersed carbonates from  $\text{CH}_4$ -bearing sediments of the HMMV caldera fall within the field of characteristic values for hemipelagic sediments, where carbonate is represented by shells and shell fragments. Authigenic carbonates from the HMMV caldera tend to plot into the field of values characteristic for typical authigenic carbonates with positive  $\delta^{18}\text{O}$ .

The carbonate buildup from the central zone of HMMV was inhabited by symbiotrophic animals

*Pogonophora* (Fig. 3), which cannot live without a methane supply and its oxidation to  $\text{CO}_2$  (Lein *et al.*, 1998; Pimenov *et al.*, 1997). Therefore, methane fluid discharge through the living buildup takes place today.

The age of carbonate carbon varies even within a single buildup, but an average age is about 10 000 yr BP (Table 4). This is not an age of  $\text{CH}_4$  carbon, as methane is undoubtedly formed in pre-Holocene sediments (Bogdanov *et al.*, 1999). Therefore, authigenic carbonates contain significant amounts of recent shell material and young seawater bicarbonate ions, formed during organic matter destruction in sediments with a considerable contribution of bacterial biomass (Pimenov *et al.*, 2000). The youngest age is determined for coral-shaped outgrowths at the buildup top.

Therefore, necessary conditions for authigenic carbonate formation exist at sites of  $\text{CH}_4$ -bearing fluid discharge, within the methane seep area in the caldera of an Arctic mud volcano, in an environment with negative temperatures and active microbiological processes.

## CONCLUSIONS

(1) Authigenic carbonates in the HMMV caldera form at sites of diffuse  $\text{CH}_4$  seepage (or more seldom bubble discharge), at the interface of  $\text{CH}_4$ -bearing sediments with bottom water.

(2) Authigenic carbonate bodies within sediments are not *in situ* formations but represent a clastic material produced during the destruction of carbonate buildups and transported by mud flows.

(3) Authigenic carbonates are formed on the seafloor during anaerobic methane oxidation by a specific microbial community, which consists of methane producers acting as methanotrophs and sulfate reducers developing on hydrogen, a product of microbial methane oxidation.

(4) Results of microbiological studies are confirmed by  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of the carbonate. Depletion of the carbonate in heavy carbon isotope  $\delta^{13}\text{C}$  is related to a formation of isotopically light carbon dioxide during  $\text{CH}_4$  oxidation, whereas a heavy isotopic composition of oxygen in the carbonate is inherited from seawater sulfate.

(5) Pertinence of authigenic carbonates to the water–bottom interface is related to the sulfate ion availability. Sulfate ion is absent within  $\text{CH}_4$ -bearing sediments. The authigenic carbonate formation ceases with the exhaustion of sulfate ion in the upper 10–20-cm layer of the  $\text{CH}_4$ -bearing sediments. Anaerobic  $\text{CH}_4$  oxidation may continue in deeper sediment layers, but here it is not accompanied by authigenic carbonate formation.

(6) Age of carbonate carbon (about 10000 yr BP) indicates a pre-Holocene, relatively young age of  $\text{CH}_4$  in the HMMV caldera.

(7) Physicochemical conditions at the water–bottom interface in  $\text{CH}_4$ -bearing sediments from the HMMV



correspond to the field of nonmagnesian calcium carbonate precipitation.

(8) Calcite, in paragenetic association with strontium barite, is the main carbonate mineral in the authigenic carbonates studied.

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# Microscopic Gold in Marine and Oceanic Sediments

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**Abstract**—The present-day contribution of coastal-marine placers into the bulk gold production is insignificant. As usual, only gold of coarse- and medium-grained classes is recovered while the fine-grained and dispersed gold are disposed into tailings. During the sedimentation, such a floating gold is removed far from the wave-surf zone. Despite the common belief about poor prospects of the Black Sea shelf for modern gold placers, we have proved the expediency to study the distribution of floating microscopic gold in Holocene marine sediments and carried out the respective works. Using the special concentrating methods, we enabled to detect the gold in most of the 830 samples collected. Geomorphological, lithological, hydrodynamic, and other factors controlling the gold potential were determined. In some cases, the gold content exceeds the minimal economic grade in continental placers. The prospective sites for further investigation were outlined. It was established that the polygenic microscopic gold can be divided into at least clastic, authigenic, and clastic-authigenic types. According to our data, the alluvial, lagoonal-marine, liman, and other sediments at the adjacent land also contain substantial amounts of microscopic gold. The preliminary study of oceanic bottom sediments near the Antarctic Peninsula and within the Argentine Basin proved the possibility of microscopic gold to accumulate under various facies conditions. The microscopic gold, mainly of clastic type, was detected here in 82% of samples. The obtained results testify to the global-scale deposition of floating microscopic gold in sedimentation basins of various age and may serve as a basis for the further comprehensive tackling of the problem in different regions.

## INTRODUCTION

It is well known that the contribution of placer gold to the bulk production of this metal is high. Before the collapse of the USSR, up to 45% of total gold was mined from placers of the country; the respective world estimate amounts to 50% (*Rossyepnye mestorozhdeniya* ..., 1997). The coastal-marine placers occupy a modest place among other economic types of placers. According to the above-cited source, coastal placers yield from 8.4% (1976–1980) to 4.3% (1986–1990) of total gold produced in Russia.

Late Quaternary alluvial or beach placers buried beneath modern marine sediments are the main type of such shelf deposits in the Arctic and Far East provinces of Russia. Traditionally, gold flakes, more than 0.25 mm in size, are recovered from beach placers by gravity separation methods, whereas the unrecoverable fine-grained and microscopic gold, as well as the finely dispersed and absorbed gold in the form of metalloorganic complexes goes into tailings. At the same time, the content of fine-grained and microscopic gold at many placer deposits reaches up to 50% and occasionally more.

In the last century, the famous metallurgist P.P. Amosov had shown that only about 1% of gold is recovered from many placers in the Urals by means of washing. According to recent data, the coarse-grained heavy gold recovered from placers amounts only to 5–10% of the bulk gold mass. Therefore, the technogenic gold accumulation in dumps of mining and processing

enterprises, including the dumps left behind the gravity separation of gold placers, can amount to 10–17% of the total production.

Thus, the prospecting of placers containing fine-grained and microscopic gold and the development of technology of its recovery became topical, especially in Ukraine, which is in need of noble metal resources. In 1993, the Laboratory of Marine Geology and Geochemistry of the Odessa State University put forward the idea concerning a possible formation of placers with fine-grained valuable minerals, first of all, gold at the vast Azov–Black Sea shelf. The point of departure for this idea is based on the following data: the long-term removal of terrigenous material from diverse rocks at the land adjacent to the Black Sea basin, the existence of subeconomic beach placers of ferrous metals and rare metals at the Black Sea shelf, the rare findings of gold and diamond grains at beaches, the geochemical haloes of gold in bottom sediments, and the theoretical consideration of transport, separation, and deposition of placer-forming minerals under transgressive–regressive regime characterizing the evolution of the Black Sea basin (Polkanov *et al.*, 1970; Sidenko *et al.*, 1979; Lunev, 1976; Lunev *et al.*, 1979). The opinions, which dominated until now, were formulated in the recent overview of mineral resources of the Black Sea (*Geologiya shel'fa* ..., 1983): the modern marine placers of the Black Sea are beyond economic interest, and the efforts should be focussed on the prospecting of buried ancient placers.

In the instructions of the State Committee of the Geology of Ukraine, we revised and summarized the data on the northwestern shelf of the Black Sea and conducted the marine expeditions. Main tasks of the investigations were as follows: (1) The elaboration of representative sampling methods of bottom sediments at the shelf and the choice of technology providing the complete recovery of fine-, microscopic, and floating flourey gold; (2) the evaluation of prospects of various morphostructural elements, both modern and buried, for the accumulation of microscopic gold in placers (deltas, beaches, spits, bars, paleoterraces, paleolimans, river paleochannels, and slightly tilted lowlands of the inner shelf); and (3) the search for productive granulometric classes of bottom sediments for the accumulation of fine-, microscopic, and flourey gold.

### RESEARCH METHODS AND SCOPE OF THE WORK

Marine field works were conducted in 1993–1996 with R/V *Topaz*, *Argon*, and *Vladimir Parshin* at the northwestern shelf of the Black Sea. The stations were irregularly positioned with a primary task to sample the geochemical haloes (up to 0.03 g/t Au) contoured in the course of the geological survey and the prospective paleogeomorphological structures outlined by the authors. The position of vessels was registered by means of the Poisk-D radiogeodetic system and the satellite navigation system with an accuracy of 50 m. Samples were taken with a PEV-4 vibropiston corer (diameter 108 mm, core pipe length 4 m) and in some cases by an Okean-0.25 dredger. In total, 590 stations were sampled during the field work, mainly at the following sites: the Odessa Bay, Sukhoi Liman, Zatoka, Zhebriyanskaya Bay, Tendra, Pradneprovskii, Odesskaya Shoal, Karkinitiskii Bay, Danube area, Zmeinyi Island area, and Sevastopol districts. The samples were mainly taken from Holocene sediments of the Black Sea Horizon, and to a lesser extent, from underlying Neoeuxinian sediments. The sampling interval was 1 m, the sea depth varied from 6 to 95 m. The sample weight was in the range from 2 to 20 kg (12 kg, on the average). All lithological varieties were sampled by fractions including those which are commonly not sampled for heavy concentrates during the geological survey at the shelf, e.g., clayey-silty and silty muds, fine silts, mixed sandy-silty-clayey sediments, and silty varieties of shelly and detrital sediments (previously considered absolutely barren).

The method of the complete recovery of all gold classes up to the gold flour was chosen on the basis of known modes of gravity separation. In the early 1960s, data were reported that testified to a high recovery of fine-grained ore minerals with spiral separators and spiral sluice boxes using the centrifugal forces in the laminar pulp flow (Ivanov, 1962; Lunev *et al.*, 1968). Subsequently, a wide range of problems concerning the concentration of fine-grained minerals under natural

conditions and the technique of heavy concentrate separation was discussed in the series of works (Lunev, 1976; Lunev and Osovetskii, 1979; Kardash, 1981). Taking all this information into account, we have dwelled on the spiral sluice box constructed by V.D. Ivanov; this device allows one to recover the heavy minerals up to 0.017 mm in size (Ivanov, 1990). At the first stage of research in two shelf areas, 41 samples were separated and amalgamated with the Goverla spiral plant constructed by V.T. Kardash. We then installed the spiral sluice box (based on the spiral sluice designed in the Irgiredmet Institute, Irkutsk) and assembled the equipment for amalgamation and desamalgamation. The free gold was extracted from the concentrate by an amalgamation; the concentrates were partly amalgamated in the Institute of Mineral Resources in Simferopol (P.I. Andreev). The sediments were analyzed by an assaying in the Laboratory of Noble and Rare Metals, Institute of Geology and Mineral Resources, Ukrainian National Academy of Sciences (A.A. Yushin). The complex of analytical methods also included the determination of moisture content, grain size analysis, mineralogical analysis, atomic absorption, etc.

After the positive analytical results had been obtained, the geological survey was placed on a broad footing in all of the above-listed areas. The preliminary results allowed the outlining of the two most prospective sites, which were sampled by a regular network of 4800 × 1600 m with a detailization to 2400 × 800 m in zones of elevated gold contents. In total, 971 samples were taken at 590 stations until 1997. In order to establish marine gold sources, including the transitional reservoirs, we also sampled 31 sections of natural and artificial exposures of the alluvial, lagoonal-marine, and liman-lacustrine sediments from the river terraces, liman terraces, and beaches in the Dniester and South Bug interfluvium. In total, 115 trench samples were taken here from Pliocene to Upper Pleistocene sandy, silty, and less frequent clayey sediments.

In order to check the hypothesis of global migration and accumulation of floating gold, we have taken and analyzed samples of bottom sediments at the shelf and continental slope of the Antarctic Peninsula and within the northern Argentine Basin. The sampling was performed on the board of R/V *Ernst Krenkel* during the first Ukrainian Antarctic Expedition in 1997. The samples of bottom sediments were taken by a gravity corer, 127 and 158 mm in diameter, and occasionally by the *Okean-0.25* dredger. Sampling stations were located in the vicinity of the Argentine Archipelago near the Ukrainian polar station *Akademik Vernadsky* (2 stations), in the Brunsfield Strait close to the Shetland Islands (2 stations) at the shelf of the South Orkney Islands (4 stations), and in the northern Argentine Basin at the latitude of Rio Grande Rise (1 station). The depth of the ocean at sampling stations was 33–250 m at the shelf, 305–808 m at the continental slope, and reached 3450 m in the Argentine Basin. The upper layer of bot-

tom sediments down to 2.6 m was sampled. The sample weight varied from 0.3 to 14.3 kg.

#### FINE-GRAINED AND MICROSCOPIC GOLD AT THE BLACK SEA SHELF

The first batch of samples taken from Odessa Bay and south of Tendra Point confirmed the almost overall contamination of bottom sediments by gold, which was detected in 31 samples, of 41; up to 20 grains were found in 13 samples and weight contents were determined in 18 samples with the highest content of 0.538 g/m<sup>3</sup> and > 0.1 g/m<sup>3</sup> in 7 samples (Lebed *et al.*, 1994; Reznik *et al.*, 1994, 1995). The further study at the shelf from the Danube mouth to Sevastopol Bay delineated the Pradnieprovskii prospective site on the floor and slopes of the paleobay of the Dnieper River that existed in early Neoeuxinian time. According to the assay results, the gold was detected in all samples. The content varies from background values (< 0.01 g/t) in 12.6% of samples to < 0.02 g/t in 40% of samples, > 0.1 g/t in 16% of samples, and > 3 g/t in 4.7% of samples (25 items). The highest content of free-amalgamated gold is 1.126 g/m<sup>3</sup>. The mean weighted (by thickness) Au content at the Pradnieprovskii site is 0.436 g/t for average thickness of 0.81 m. The sites of the Odessa Bay, Tendra, and others turned out to be less promising. Nevertheless, the distinct anomalous zones with a total area of a few hundred square kilometers were outlined by an isoline of 0.2 g/t at five sites. Most of such zones are related to remnants of old river and liman terraces overlain by Holocene marine sediments and flooded river channels. The potential gold and associated noble metal resources were estimated in the anomalous zones.

The sampling of modern and ancient river and liman terraces on the land also resulted in findings of microscopic gold in alluvial and liman sediments; the Au content reaches 0.155 g/m<sup>3</sup> (0.380 g/t, according to the assay results) in the Dniester basin, 0.053 g/m<sup>3</sup> (0.120 g/t, according to the assay results) in terraces of the South Bug. In general, the gold potential of terrigenous sediments is lower than that of the marine sediments.

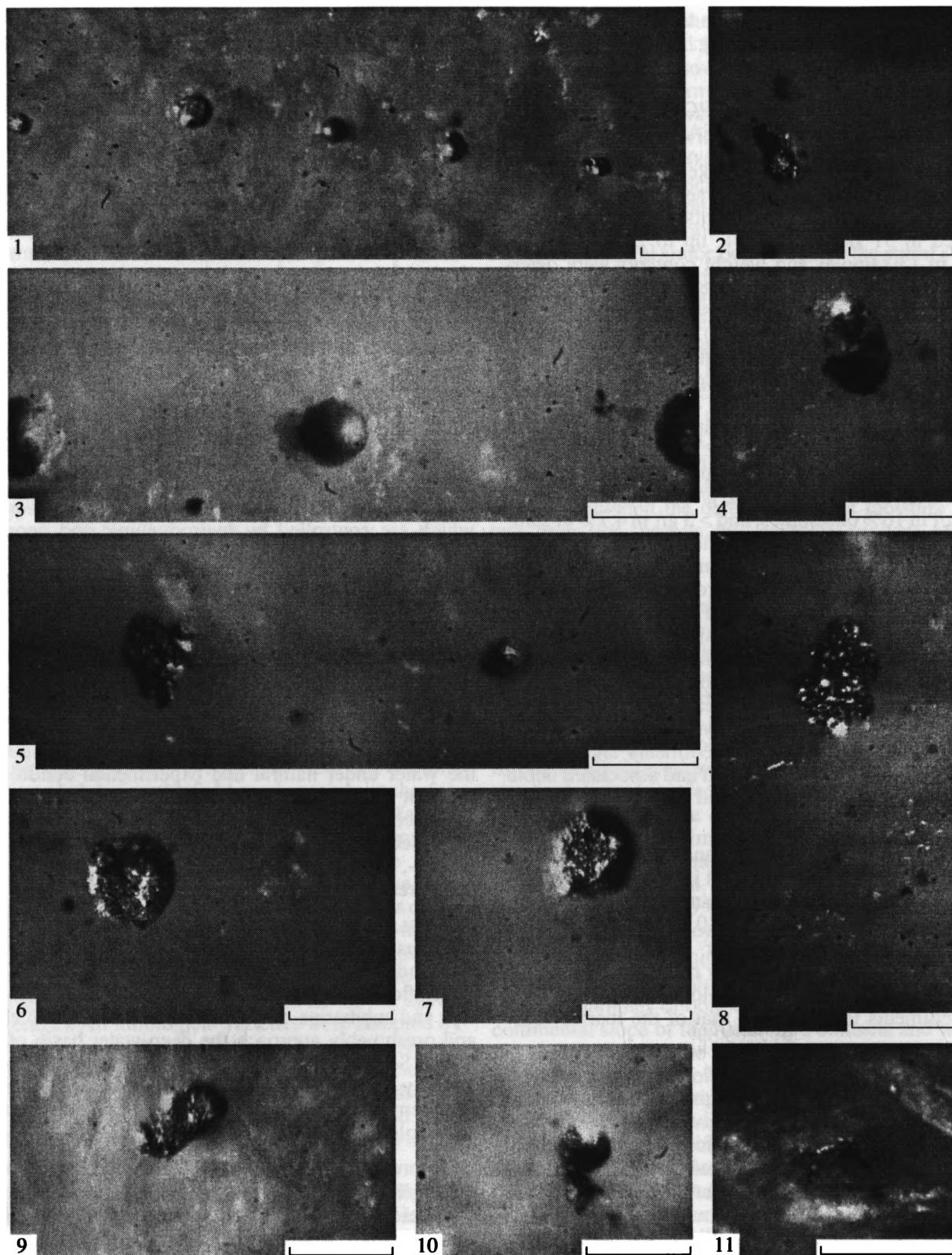
Based on results of field and analytical investigations, we suggested that a new prospective economic type of gold placers exists at shelves of the seas washing the Ukraine. The placer-forming fine-grained, microscopic, and floury gold is fixed throughout the sampled section of Holocene sediments and in Meotian (?) sediments at a depth down to 28 m beneath the bottom (Lebed *et al.*, 1994; Reznik *et al.*, 1994). Taking into account the elevated Au contents in continental facies, it may be assumed that the Azov–Black Sea gold placer province at the southern slope of the Ukrainian Shield covers both the shelf and adjacent land. Almost half of the samples contain Pd (0.125–0.200 g/t, according to the assay results) and other impurities unusual for gold.

The problem concerning the forms of transport and the accumulation of gold under marine conditions beyond the limits of its common concentration in alluvial, deltaic, liman, and beach placers cannot be settled without the account of all geological, mineralogical, hydrodynamic, and physicochemical factors of sedimentation. At the current stage of the study, we can state that microscopic gold placers within the periodically flooded and drained shelf are distal deposits of floating gold, which accumulates in recent and Pleistocene marine sediments in the offshore environment; the gold deposition is mainly controlled by morphostructural and related hydrodynamic factors. Most stations with a high gold content are related to submarine river valleys, flooded limans, rivermouths and terraces, as well as to bottom depressions within the flat inner shelf with a stagnant hydrodynamic regime. We suggest that the placers of fine-grained and microscopic gold cannot be formed in the zone of active wave-surf processes or during the transport of sediments along the coast. The floating gold is removed into relatively deep parts of the shelf and deposited in sedimentation traps, which are controlled by hydrodynamic and geomorphological factors.

The lithological control of the gold distribution is also evident. The highest gold content is related to poorly sorted shelly clayey–silty–sandy sediments. The gold content regularly decreases with sediment sorting (more active geodynamic regime) and the transition from four-component to one-component sediments of psammitic grain size. This is consistent with the behavior of fine- and microscopic gold during its transport in the water under natural and experimental conditions. (Shpunt and Shamshina, 1977; Kardash, 1981; Koval'chuk, 1994). It was established that the increased density of the medium promotes the transport of fine-, microscopic, floury, and finely dispersed gold for a great distance.

Thus, it should be expected that such gold, along with suspension, would be transported by river water for hundreds of kilometers toward the outer shelf. Turbidity flows may transfer the gold along the paleovalleys and submarine canyons over the continental slope and presumably approach the deep-water basin of the Black Sea. The transport of dissolved and colloidal gold by river water is virtually unrestricted; various geochemical barriers promote the transformation of such gold into a mineral form.

In order to study specific features of gold in detail, its largest particles were singled out from the concentrate before the amalgamation. The smaller grains close in size to the limit of visual detection were selected from the filters under the binocular microscope after the desamalgamation. The gold is mainly related to the classes varying from fine-grained to the floury; the grain size ranges from 0.005 to 0.5 mm; grains of 0.01–0.03 mm in size are predominant (Fig. 1). Some amount of gold is probably related to the class of



**Fig. 1.** Shape of gold grains from bottom sediments at the Black Sea shelf. (1–8) Tendra Point district; (4) grain with a quartz inclusion, 0.01–0.02 mm in size; (9, 10) escarpments of the Tiligul Liman; (11) Dnieper paleovalley. Scale bar 0.1 mm.



< 0.005 mm, but this class is only guessed under a microscope. The shape of gold grains is an important indication of their origin and mode of transport. The study of more than 300 gold grains has shown that at least three morphogenetic classes of gold may be recognized (Reznik and Zrellov, 1997): (1) Clastic (terrigenous) gold as rounded, flattened grains occasionally with quartz intergrowths; (2) authigenic gold as particles of perfectly spherical, tablet- or clusterlike shape and with signs of the *in situ* growth; and (3) clastic-authigenic gold with the indication of the subsequent metal growth over clastic particles at the postsedimentation stage.

Some observations indicate that the gold of other (biogenic, microbial, submarine hydrothermal, technogene, etc.) genetic types also may exist. The above-mentioned mechanisms of migration and deposition of the gold related to nontraditional (authigenic, biogenic, etc.) genetic types are consistent with the reported data on the high migration ability of gold in the supergene zone where it is transported as finely dispersed particles, along with true and colloidal solutions (Pashkova *et al.*, 1988; Tauson *et al.*, 1989; Tsar'kova *et al.*, 1993). The deposition of the gold as native particles occurs at geochemical barriers of river-sea type, under effect of organic matter, as well as a result of microbial processes, selective coagulation, breakdown of organometallic complexes, and absorption by iron hydroxides.

#### MICROSCOPIC GOLD IN BOTTOM SEDIMENTS OF THE ANTARCTIC SHELF AND IN OCEANIC SEDIMENTS

The above-described mechanisms of migration and deposition of microscopic and flourey gold act at every geological time and are characteristic of any water basin independent of age and geographic setting. In the Antarctic region, we have dredged mainly mixed, glacial-marine sediments represented by siliceous (diatomaceous) clayey-silty oozes enriched in terrigenous clastic sandy-gravel-pebble material derived from the disintegration of volcanic, pyroclastic, and intrusive rocks exposed at the adjacent land; the psammitic fraction includes a substantial amount of dark-colored and ore minerals. A small amount of biogenic carbonates is pointed out. Oceanic sediments in the Argentine Basin are represented by biogenic calcareous (foraminiferal) ooze and terrigenous mud.

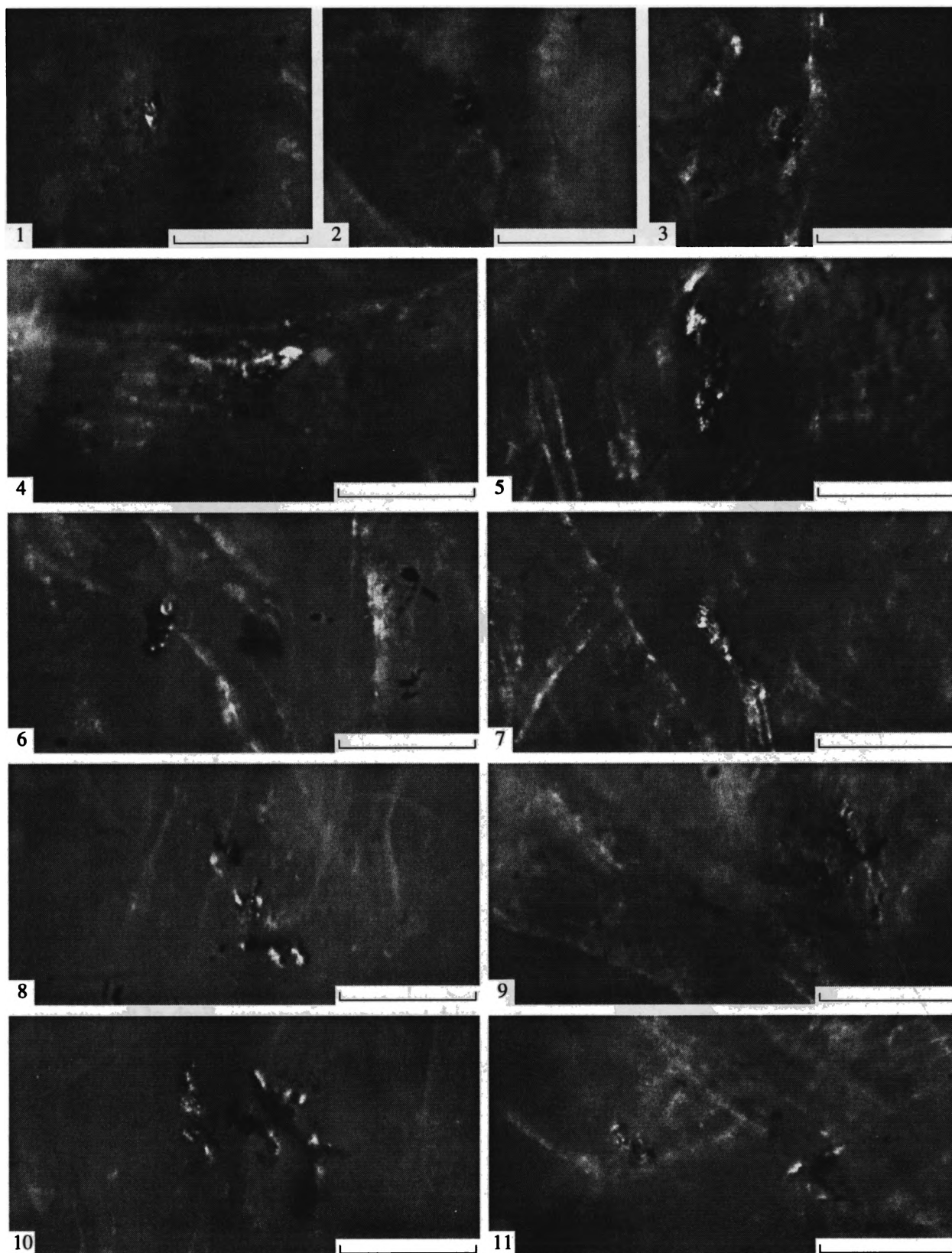
After the gravity separation of Antarctic sediments with a spiral sluice box and the subsequent amalgamation of concentrates, the free gold, visible under a microscope with a 30-fold magnification, was detected at 8 of 9 stations (in 9 of 11 concentrates). The moderate amalgamation regime allowed the preservation of the morphology of gold grains and the decipheration of their origin and ways of transport. From one to nine gold grains, 0.017–0.110 mm in size, as well as plenty of tiny fragments close in size to the optical detection limit were found in each sample. The shape of gold

grains is drastically distinct from that of gold from the Black Sea shelf. Fusiform, dendritic, and tabular grains are predominant; tablets and grains with irregular edges were also encountered (Fig. 2). Relics of crystalline forms, i.e., clearly visible faces, were noticed in some grains. The gold is obviously terrigenous; however, there are virtually no signs of transportation. This most likely indicates the transport of gold grains by ice and their derivation from neighboring provenances. The morphology of gold grains from different districts reveals some specific features.

For example, one sample, taken close to the *Akademik Vernadsky* station and represented by a terrigenous carbonate-free clayey-silty mud with chippings, in the interval of 0–0.25 m, contains the fusiform gold, about 0.030 mm in size. This sample is also distinguished by a high content of heavy fraction (up to 26.8 kg/m<sup>3</sup>) and the highest magnetite content (up to 3.74 kg/m<sup>3</sup>).

In the deep-water trench of the Brunsfield Strait south of the South Shetland Islands, two samples of bottom sediments were taken from depths of 590 and 750 m; intervals of sampling were 0–0.25 and 0–1.45 m, respectively. The sediments consist of clayey and clayey-silty muds with rock fragments and bear indications of rewashing, redeposition, and gaseous vugs; all this indirectly testifies to the variable hydrodynamic regime. Three gold grains of tabular, flaky, and rounded shapes with hollows were found in the sample, only 0.3 kg in weight. The morphology of grains may be a result of their distant transport. The dimensions of gold grains are 0.033 × 0.017 mm, 0.042 × 0.012 mm, and 0.042 × 0.021 mm. A high Au content may be expected at that site; the preliminary estimation based on three gold grains yields the Au grade not lower than 0.1 g/t. Nine tabular gold grains with lacerated (jagged) margins were extracted from the sample, 14.3 kg in weight; their size varies from 0.033 to 0.050 mm. The dendritic gold, more than 0.040 mm in size, was also detected herein. The heavy fraction content reaches 20 kg/m<sup>3</sup> and the magnetite content research 3.09 kg/m<sup>3</sup>. In the vicinity of South Orkney Islands, the samples were recovered from a depth of 125–808 m. The sediments are represented by clayey and silty muds with terrigenous fragments. Each of the four samples (5.0–12.7 kg in weight) contained 2 to 6 gold grains, 0.017–0.110 mm in size. The gold grains are dendritic and tabular in shape with lacerated edges and a shagreen surface. One grain reveals a distinct crystalline face. The heavy fraction content reaches 34 kg/m<sup>3</sup>, the magnetite content is 1.56 kg/m<sup>3</sup>.

The adjacent land of the Antarctic Peninsula and the Scotia volcanic arc is related to the West Antarctic Fold System, which is a part of the Pacific Mobile Belt. The basement of the Scotia volcanic arc is composed of Upper Paleozoic metamorphic rocks, which are overlain by Jurassic silicic volcanics. At the Argentine Archipelago (*Akademik Vernadsky* station), acid and intermediate volcanic and pyroclastic rocks are



**Fig. 2.** Shape of gold grains from bottom sediments at the Antarctic shelf and in the Argentine Basin. (1–7) vicinity of South Orkney and South Shetland Islands; (8–11) Argentine Basin. Scale bar 0.1 mm.

intruded by Cretaceous granitoids. Numerous faults and fracture zones; the other occurrences; the bleaching, silification, and pyritization of rocks; and abundant quartz and pegmatite veins, occasionally with magnetite, hematite, and sulfide pockets, up to 20 cm in diameter, were observed during the reconnaissance geological routes at the Argentine Islands and at the coast of Antarctic Peninsula (Reznik, 1997). Such ore occurrences likely serve as a source of magnetite for sediments sampled. Other valuable heavy minerals might have been gained in a similar way.

The abundant gold in samples under study indicates that the region with an intense tectonic and magmatic activity stands out as a possible provenance of microscopic marine gold and, thus, requires a special study aimed at the primary gold mineralization.

In the northern Argentine Basin, the bottom sediments were recovered from a depth of 3450 m. The interval of sampling was 2.6 m; the sediments are represented by clayey and silty-clayey muds. They vary along the section from the biogenic foraminiferal calcareous ooze (interval 0–0.4 m) to the completely carbonate-free gray terrigenous mud (with hydroillite spots) separated by an erosional surface, which likely corresponds to a hiatus. Sixteen fusiform and dendritic shape gold grains, from 0.010 to 0.070 mm in size (Fig. 2), were found in two samples, 5.2–6.6 kg in weight. The amount of gold grains increases downward the section. The approximate Au content in the lower interval is estimated at 0.055 g/t. The study of heavy fraction under a binocular microscope has shown that the active replacement of organic remains by pyrite and iron hydroxides is observed in the lower interval. This might have been induced by a change of physicochemical conditions as a result of periodical submarine discharge of hydrothermal solutions. The exclusive fusiform and dendritic shapes of gold grains, which are distinct from the tabular grains with lacerated margins in the Antarctic Peninsula region; the absence of gold grains with signs of terrigenous provenance; a great depth of ocean; and previously suggested good prospects of the Rio-Grande Rise for the formation of hydrothermal ore suggest possible genetic relations of gold to submarine hydrothermal discharge.

## CONCLUSIONS

The accumulations of fine-, microscopic, and flourey gold, which have been reported from the Black Sea shelf, are not purely a local phenomenon inherent in a certain province with specific features. Most likely, this process is governed by global regularities, mainly, by gold removal from adjacent provenances (erosion or glacial transport as in the case of Antarctica), the eustatic oscillations in the sedimentation basin, and the alternately active hydrodynamic regime with stagnant gyre-type structures, the existence of geomorphological traps favorable for the gold deposition, and the

geochemical barriers where the dissolved or colloidal gold is transformed into mineral forms.

As follows from our study, the Au content in bottom sediments reaches and exceeds the minimal economic grade in continental placers. Thus, the problem concerning the microscopic marine gold is not only of scientific but also of applied interest. It should be taken into account that the development of marine gold deposits does not require the alienation of deficient territories, the distortion of landscape and their recultivation after the mining, the demolishing of buildings, and the buildup of roads and other infrastructure. The mining of ore is also simplified due to the absence of overburden and mines. The Au-bearing bottom sediments will be mined immediately as a disintegrated material, and the technology of metal recovery will be considerably simplified and improved by an application of modern gravity separation and flotation.

Thus, the further purposeful prospecting for placers of microscopic marine gold is an urgent issue for many regions. The primary tasks to be solved comprises the theoretical modeling of transport and concentration of microscopic, dispersed, colloidal, and dissolved gold under marine conditions; the detailed study of ore-controlling geomorphological, hydrodynamic, hydrochemical, lithological, facies factors, etc. It is necessary to revise the data on placer formation at shelves of basins (both modern and ancient) and the adjacent land. Additionally, we should introduce the advanced methods of prospecting, sampling, and processing into the practice of geological exploration.

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# Manganese Hydroxides in Alluvium as an Example of Aquagene Mineral Formation<sup>1</sup>

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**Abstract**—We found and studied the phosphate and ferromanganese mineralization in the Holocene alluvium at upper reaches of the Severnaya Dvina River. Possible sources and accumulation mechanisms of manganese during the aquagene-fluvial hydroxide formation are first discussed.

At present, the alluvial ferromanganese mineralization represents a poorly studied aspect of manganese ore formation. The study of fluvial mineralization, which strongly resembles the economic manganese ores in terms of mineralogy and is formed at present-day rivers, may significantly contribute to the refinement of geochemical theory (Strakhov, 1968) and serve as a basis for the study and estimation of numerous paleoanalogues.

Alluvial manganese deposits were known at least since the late 19th century (Krotov, 1954), but, up to now, their investigations were rare and cursory (Churakov, 1944; Kavitskii *et al.*, 1980; Mkrtych'yan *et al.*, 1979; Nikol'skaya, 1962; Segnit, 1984). There are only two works that attempted to explain the ways of manganese accumulation in river sands (Chernov, 1944; Hewett, 1916). However, these works used traditional viewpoints, which assumed a direct sedimentation of manganese hydroxides from the meteoric waters. This prevented the elucidation of genetic specifics of the alluvial mineralization.

## STUDY OBJECTS

Our investigations were carried out in upper tributaries of the Severnaya Dvina River, which are located between zones of moderate and high fluvial ion outflows (Alekin and Brazhnikova, 1964). We studied two typical profiles of alluvial soils, which host horizons enriched in manganese hydroxides. The first profile crops out in the left steep bank of the Vychegda River, 4.3 km east of the settlement of Ust Lokchim, and represents high floodplain deposits. The second profile is located in the low right bank of the Sysola River, at the latitude of the settlement of Ib, and represents low floodplain deposits. Both studied profiles are restricted to abrupt bendings of the corresponding rivers.

**Profile 1 (Vychegda River).** It traces the coastal ferromanganese horizons over 100–150 m. Downward to the water edge, the profile can be divided into the following horizons (Fig. 1):

(1) Detritus and turf soil horizon; thickness 10–15 cm.

(2) Forest soil composed of brownish gray, weakly ferruginous loams; the lowermost part consists of discontinuous horizons of bog peat; thickness 20–90 cm.

(3) Grayish beige soil loams and clays with ferruginous spots. The upper part of horizons contains abundant plant and root fragments covered by brownish clayey material; thickness 40–80 cm.

(4) Gray and dark gray loams and sandy loams with a minor manganese hydroxide dispersion (Mn-rich horizon 1); thickness 5–10 cm.

(5) Grayish brown sandy loams with veined-lumpy aggregates of blue iron phosphates; the lower part of horizon exhibits crossbedding; the sandy loams are occasionally replaced by bluish gray plastic loams; thickness 40–90 cm.

(6) Sands partially cemented by ferromanganese hydroxides (Mn-rich horizon 2); they are brownish-black, nodular, and friable; thickness 10–50 cm.

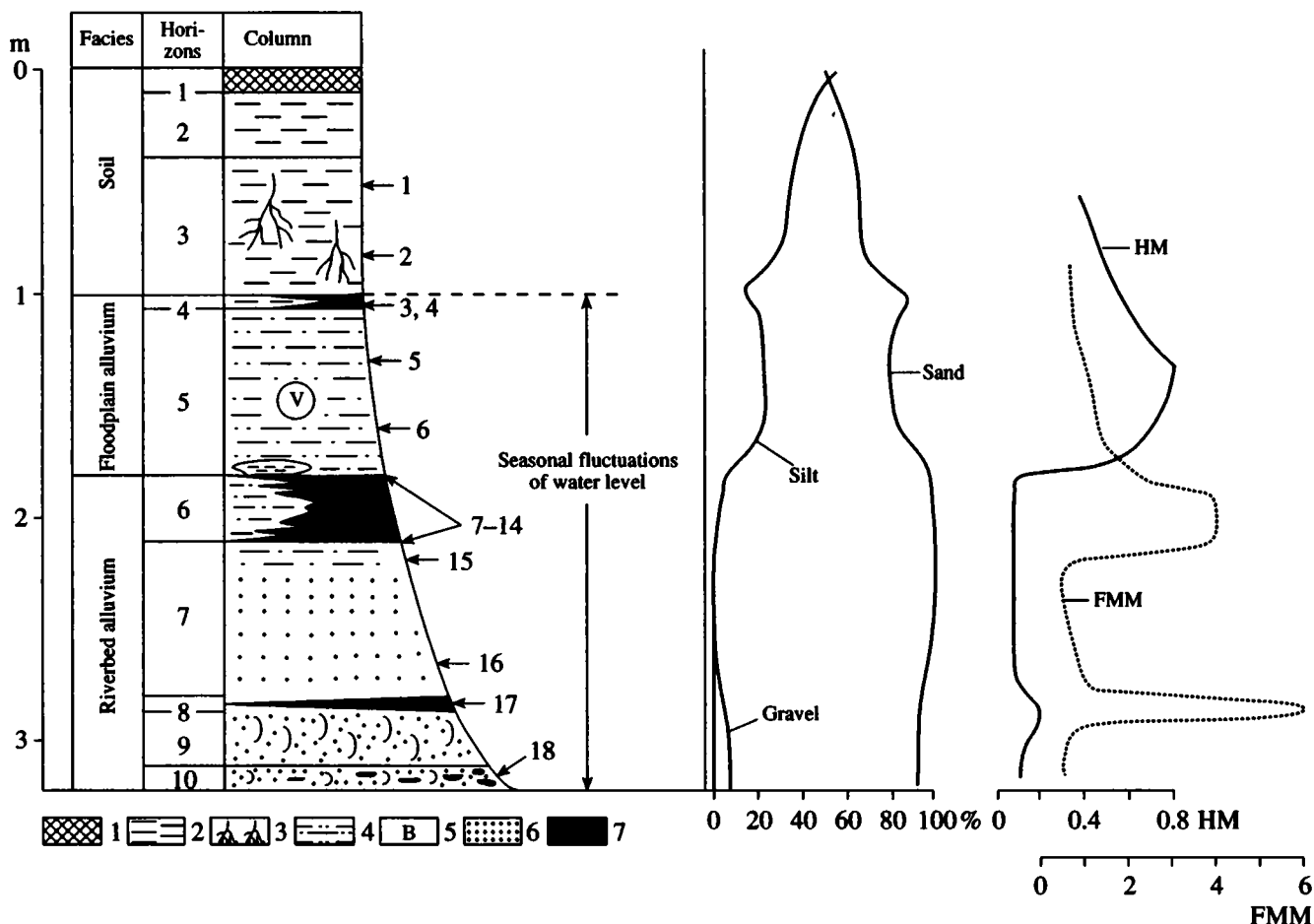
(7) Brownish, crossbedded sandy loams rapidly grading into gravelly, irregularly ferruginous grayish and light brown sandstones; at the base, the horizon contains 30–40% of gravel; thickness 60–80 cm.

(8) Brownish and dark gray sands partially cemented with ferromanganese hydroxides (Mn-rich horizon 3); the blocks of lithified sands are separated by looser, highly ferruginous sands with poorer manganese mineralization; thickness 1–5 cm.

(9) Light gray, commonly crossbedded sands; thickness 30–40 cm.

(10) Lens-like and crossbedded, weakly ferruginous sandy loams with an irregular (sporadic) dispersion of manganese oxide (Mn-rich horizon 4); thickness 5–25 cm.

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**Fig. 1.** Scheme of a soil-alluvial profile with horizons of aquagene manganese mineralization. The arrows show the sampling points. (1) Turf, (2) loam, (3) remnants of plant roots, (4) sandy loam, (5) vivianite mineralization, (6) sand, (7) horizons of oxide manganese mineralization. HM (hydromica module) =  $3\text{Al}_2\text{O}_3/(\text{SiO}_2 + 2\text{Al}_2\text{O}_3)$ . FMM (ferromanganese module) =  $(\text{Fe}_2\text{O}_3 + \text{FeO} + \text{MnO}_2 + \text{MnO})/(\text{TiO}_2 + \text{Al}_2\text{O}_3)$ .

The total thickness of profile 1 is 2.5–4 m. Based on a facies analysis, the profile may be divided into three zones (from top to bottom): soil-bog (horizons 1–3), alluvial-floodplain (4–5), and alluvial-riverbed (6–19).

The approximate thickness ratio of distinguished zones is 1.5 : 1 : 2. By analogy with dated sediments of the Vychegda River (Marchenko and Duryagina, 1996), the age of studied alluvium may be determined as the Middle Holocene (8000–2300 yr).

**Profile 2 (Sysola River).** It extends for 50 m up to the disappearance of manganese hydroxide mineralization in the alluvial sands. Downward to the water edge, the profile is represented by the following horizons:

(1) Meadow turf; thickness 5–10 cm.

(2) Yellowish gray, slightly ferruginous sands; thickness 20–40 cm.

(3) Grayish yellow, occasionally ferruginous gravelly sands; thickness 10–20 cm.

(4) Brownish gray gravelly sands with dispersed manganese oxide mineralization (Mn-rich horizon); thickness 10–15 cm.

(5) Light gray, crossbedded sands; thickness 5–10 m.

The total thickness of the described sediments ranges from 0.5 to 1 m. In terms of facies, all but the uppermost turf horizon belong to riverbed alluvium.

## LITHOLOGY AND MINERALOGY OF SEDIMENTS

Facies zones, which were distinguished within the Mn-rich soil-alluvial profiles, differ in granulometry and composition (Tables 1, 2).

**Soils** are represented by hydromica- and quartz-bearing silts, which chemically may be attributed to oxidized moderate-Fe silicites with subordinate siallites. The normative content of hydromica component is less than 50%. Manganese occurs in clark amounts.



**Table 1.** Granulometric composition (%) of sediments in the soil-alluvial profiles at floodplains of the Vychehda and Sysola rivers

| Profile location                | Horizon | Samples | Fractions, mm |         |       |        |     | Sediments           |
|---------------------------------|---------|---------|---------------|---------|-------|--------|-----|---------------------|
|                                 |         |         | <0.1          | 0.1–0.5 | 0.5–1 | 1–3    | >3  |                     |
|                                 |         |         | Silt          | Sand    |       | Gravel |     |                     |
| Vychehda River, high floodplain | 3       | 1       | 100           | –       | –     | –      | –   | Silt and silty sand |
|                                 | 3       | 2       | 32.2          | 35.4    | 31.7  | –      | –   | –                   |
|                                 | 4       | 3       | 10.2          | 42.2    | 47.6  | –      | –   | Silty sand          |
|                                 | 5       | 4       | 21.4          | 41      | 37.6  | –      | –   | Silty sand          |
|                                 | 5       | 5       | 18.8          | 22      | 59.2  | –      | –   | –                   |
|                                 | 6       | 6       | 1.8           | 44.3    | 53.9  | –      | –   | Sand                |
|                                 | 7       | 7       | –             | 65.1    | 25    | 9.6    | 0.3 | Gravelly sand       |
| Sysola River                    | 8–10    | 8       | 2.1           | 85.5    | 0.9   | 4.4    | 7.1 | –                   |
|                                 | 2       | 9       | –             | 94.4    | 5.6   | –      | –   | Sand                |
|                                 |         | 10      | –             | 90.7    | 9.3   | –      | –   | –                   |
|                                 | 3       | 11      | –             | 81.9    | 10.3  | 5.3    | 2.5 | Gravelly sand       |
|                                 | 4       | 12      | –             | 11.2    | 82.5  | 3      | 3   | –                   |

Note: (–) not detected.

The soil horizon is relatively enriched in  $C_{org}$  (on the average, up to 0.28%).

The most specific component of these rocks are cone-shaped and tubular bodies with thin axial channels, which contain fragments of dry plant remnants (Fig. 2). Such formations in the paleosols are often considered as “pedorelics” (Feofilova *et al.*, 1981), i.e., the pelitomorph mineral products of plant activity inherited from soils.

The studied samples consist of the clayey material with an irregular extinction, colorless center, and Fe-rich rim. The tubular bodies mainly consist of highly hydrated hydromica-type phases and practically X-ray amorphous allophanoids of a Fe–Al–P–Si composition (Table 3). Both these phases may be ascribed to so-called mutabilites (Gritsaenko, 1946; Kukovskii, 1983). In addition, the pelitic component contains individual, relatively large (to 100  $\mu$ m) inclusions of anhydrous Ti–Fe compounds compositionally similar to pseudobrookite.

The floodplain alluvium consists of quartz- and hydromica-bearing silty sands, which chemically correspond to ferruginous siallites. As compared to the above soil silts, the considered sediments are characterized by a higher hydromica content, somewhat lower oxidation, and Mn content considerably higher than the Clarke value (Table 2). The  $C_{org}$  content in this horizon sharply decreases to 0.015%.

This horizon contains lumps and pockets of blue iron phosphates. In appearance, they are cryptocrystalline and earthy. However, the electron microscopy shows that phosphates are represented by aggregates of prismatic crystals of 2–5  $\mu$ m in size. An equant appearance of grains is defined by  $m\{110\}$  and  $a\{100\}$  monoclinic prismatic faces. The tabular forms consist of  $b\{010\}$  pinacoid faces.

Based on X-ray powder diffraction data, the considered phosphates are identified as vivianite with following unit cell parameters ( $\text{\AA}$ ):  $a_0 = 10.00\text{--}10.12$ ,  $b_0 = 13.71\text{--}13.84$ ;  $c_0 = 4.67\text{--}4.7$ ;  $\angle\beta = 104.43\text{--}104.47^\circ$ . Infrared absorption spectra contain the bands of asymmetric deformation oscillations (460–470, 515–520, 580–590  $\text{cm}^{-1}$ ) and split bands of stretching oscillations (1030–1040, 1090–1100  $\text{cm}^{-1}$ ) of phosphate radical, and broad OH-stretching regions (1635–1640, 3450–3460  $\text{cm}^{-1}$ ). The shift of most mentioned bands to the long-wave region and splitting of the  $\nu_3$  band may indicate the isomorphous substitution in the  $[\text{PO}_4]$  radical.

A microprobe analysis (Table 4) indicates that the studied phosphates are characterized by a universal presence of Si impurity and equiatomic ratio of octahedral cations to phosphorus (+Si). Based on these and IR data, the crystallochemical formula is  $\text{Me}_6[(\text{P}, \text{Si})\text{O}_4]_6 \cdot n\text{H}_2\text{O}$ . The latter differs considerably from the formula reported for the vivianite–kerchenite series (Chukhrov

**Table 2.** Chemical composition of sediments and ores of the soil-alluvial profile, the Vychegda River

| Components                     | Soil (3)   |       | Floodplain alluvium (3) |       | Riverbed alluvium (5) |       | Mineralized riverbed alluvium (9) |       |
|--------------------------------|------------|-------|-------------------------|-------|-----------------------|-------|-----------------------------------|-------|
|                                | 1          | 2     | 1                       | 2     | 1                     | 2     | 1                                 | 2     |
| SiO <sub>2</sub>               | 59.48–68.9 | 65.43 | 55.26–58.6              | 56.66 | 88.22–94.48           | 92.26 | 53.34–89.18                       | 81.29 |
| TiO <sub>2</sub>               | 0.66–0.83  | 0.77  | 0.79–0.83               | 0.8   | 0.12–0.36             | 0.21  | 0.14–0.3                          | 0.21  |
| Al <sub>2</sub> O <sub>3</sub> | 9–12.41    | 11.17 | 11.46–13.4              | 12.57 | 1.87–4.22             | 2.68  | 1.92–5.37                         | 2.76  |
| Fe <sub>2</sub> O <sub>3</sub> | 4.45–13.48 | 8     | 5.14–8.53               | 7.33  | 0.81–2.2              | 1.32  | 1.11–18.25                        | 5.28  |
| FeO                            | 0.66–0.86  | 0.78  | 1.64–4.26               | 3.01  | 0–0.2                 | 0.07  | 0–0.31                            | 0.03  |
| CaO                            | 0.48–0.83  | 0.64  | 0.46–0.83               | 0.67  | 0.35–0.48             | 0.42  | 0.39–0.82                         | 0.58  |
| MgO                            | 1.01–1.21  | 1.12  | 1.1–1.3                 | 1.2   | 0–0.33                | 0.15  | 0–0.41                            | 0.22  |
| MnO                            | 0.03–0.28  | 0.14  | 0.19–1.34               | 0.91  | 0.06–0.75             | 0.34  | 0–1.04                            | 0.47  |
| MnO <sub>2</sub>               | –          | –     | –                       | –     | –                     | –     | 0–12.45                           | 4.57  |
| Na <sub>2</sub> O              | 1.07–1.41  | 1.23  | 0.92–1.07               | 1.01  | 0.26–0.76             | 0.41  | 0.37–0.73                         | 0.47  |
| K <sub>2</sub> O               | 1.52–2     | 1.74  | 1.48–1.65               | 1.55  | 0.5–1.1               | 0.72  | 0.51–0.96                         | 0.62  |
| P <sub>2</sub> O <sub>5</sub>  | 0.43–2.21  | 1.05  | 1.47–2.22               | 1.72  | 0.04–0.06             | 0.05  | 0.03–0.25                         | 0.11  |
| CO <sub>2</sub>                | 0.09–0.22  | 0.16  | 0.34–2.68               | 1.52  | 0.02–0.75             | 0.25  | 0.16–0.75                         | 0.43  |
| H <sub>2</sub> O               | 2.31–4.11  | 3.01  | 3.41–3.91               | 3.73  | 0.15–0.51             | 0.33  | 0.28–2.47                         | 0.91  |
| Mn                             | 0.02–0.29  | 0.18  | 0.31–1.03               | 0.76  | 0.05–0.58             | 0.26  | 0.12–6.16                         | 3.24  |
| Fe                             | 3.63–10.12 | 6.21  | 4.88–9.29               | 7.48  | 0.68–1.7              | 0.98  | 0.78–12.78                        | 4.16  |
| Cu                             | 10–30      | 20    | 0–30                    | 17    | –                     | –     | 0–40                              | 4.5   |
| Zn                             | 60–160     | 90    | 40–160                  | 95    | 20–30                 | 22    | 10–160                            | 35    |
| Co                             | 10–50      | 30    | 0–50                    | 30    | 0–30                  | 6     | 0–30                              | 10    |
| Ni                             | 50–80      | 65    | 10–80                   | 60    | –                     | –     | 10–80                             | 35    |
| MnO <sub>2</sub> /Mn           | 0          | 0     | 0                       | 0     | 0                     | 0     | 0–1.59                            | 1.2   |
| HM                             | 0.36–0.46  | 0.43  | 0.58–0.68               | 0.65  | 0.04–0.09             | 0.06  | 0.04–0.22                         | 0.07  |

Note: Oxides in wt %, trace elements in ppm; (1) variation ranges; (2) average; the number of analyses is in parentheses. Hydromica module (HM) =  $3\text{Al}_2\text{O}_3/(\text{SiO}_2 + 3\text{Al}_2\text{O}_3)$ .

and Ermilova, 1956; Simonen, 1986); however, it agrees well with our investigations.

Thus, the floodplain alluvial deposits of the Vychegda River contain vivianite-like three-valent iron phosphate, i.e., oxykerchenite. The mentioned stoichiometry of this mineral (equiatomic ratio of cations and anions) may be explained by authigenic origin of oxykerchenite. The deficiency of positive charges (3–10%) in the calculated empirical formulas of this mineral indicates a possible presence of  $\text{H}_3\text{O}^+$  groups.

The transition to the **riverbed alluvium** is accompanied by a sharp change of sediment types. This zone mainly consists of granulometrically uniform, nearly

quartzose sands with occasional subordinate (2–5%) gravels. Compositionally, these sediments correspond to ferruginous, extremely oxidized silicites. Horizons enriched in manganese hydroxides are mainly restricted to individual intervals of ferruginous, floodplain, gravelly sands (Fig. 1).

#### STRUCTURE AND COMPOSITION OF THE FERROMANGANESE MINERALIZATION

The studied horizons enriched in manganese oxides are represented by stratal bodies, which consist of loose, partially lithified brownish-black sediments.

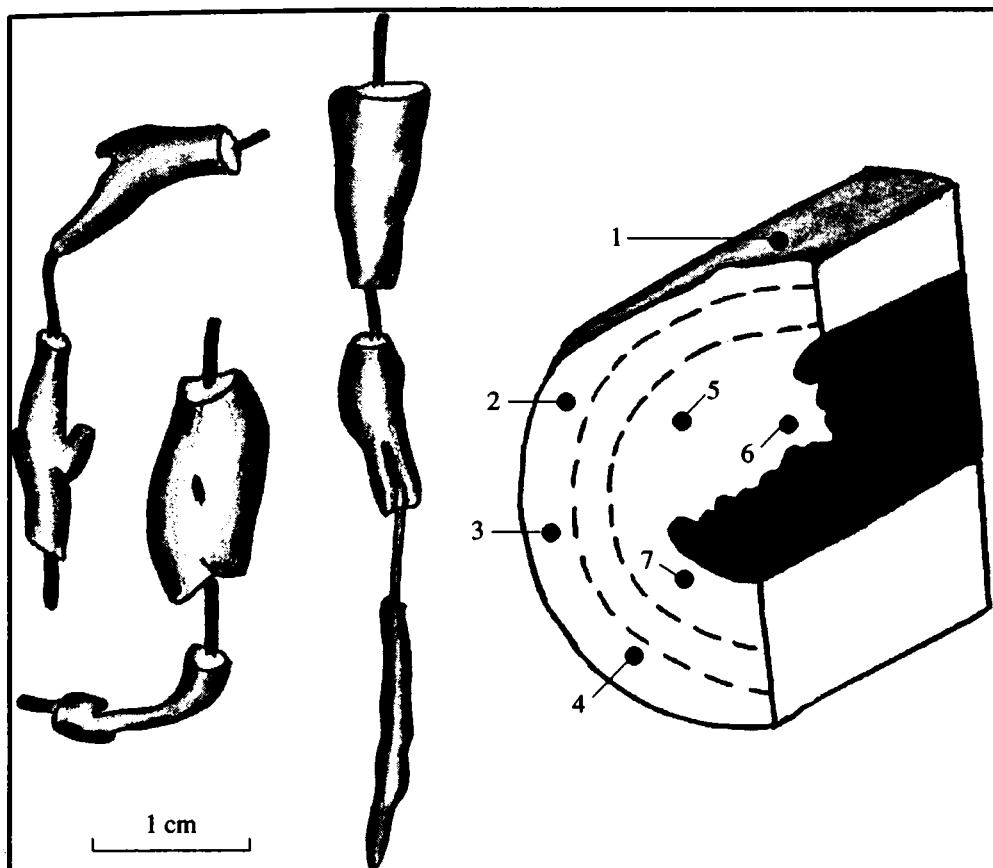


Fig. 2. Near-root tubular bodies from the soil-alluvial profile at the Vychehda River. (1–7) points where mutable phases were determined (the point numbers correspond to ordinal numbers of analyses in Table 3).

These bodies continuously extend along the river shore and are gradually thinned out downstream and upstream. The bed thickness reaches 40–50 cm. The major Mn-rich bed reveals the variable stratigraphic position in the floodplain sand sequence. This distinctly suggests the epigenetic origin of the considered mineralization.

Landward, the beds are separated into lenticular bodies thinning out at a distance of 40–100 cm (Fig. 3). The thinning out is characteristic of manganese mineralization in alluvial deposits (Chernov, 1944). The measurements showed that the landward extension of ore horizons has a positive correlation with their thickness. The ratio of these parameters shows narrow variations from 3 to 8.

The studied oxide mineralization occurs as secondary crustified cement developed as films and thin crusts on terrigenous grains (Fig. 4). The cementation gradually develops from the formation of individual agglutinates (botryoidal aggregates of several grains). The oxide films range from 10–20  $\mu\text{m}$  to 2–3 mm in thickness. The crust surface has an uneven relief, which is typical of polyspheroidal (“sintered”) aggregates. In cross-section, the oxide crusts are characterized by a negative correlation between Fe and Mn ( $r = -0.6$ ).

Outward the crusts, the Fe content decreases to practically complete disappearance, while the Mn content increases. The mentioned opposite behavior of Fe and Mn is well consistent with the distinct replacement of the earlier iron hydroxides by the later manganese hydroxides.

The studied mineralization consists of weakly crystallized, commonly semi-amorphous manganese and ferromanganese oxyhydroxides. In X-ray powder diffraction images, manganese phases are expressed in two fairly broad diffuse bands with maximums at 10–14 and 20–25°. In the IR spectra, these phases are identified as individual diffuse bands at 470 and 550  $\text{cm}^{-1}$ . Based on these data, this phase may be recognized as vernadite. The accurate diagnostics of iron oxides is also strongly complicated owing to their poor crystallinity. However, based on a fine-flaky appearance of grains in thin sections, they may be supposedly identified as feroxyhyte.

The composition of ferromanganese hydroxides was studied with an X-ray method (Table 4). The obtained data indicate the development of two mineral series in the studied alluvial deposits (Fig. 5). The first series includes the intermediate products of feroxyhyte replacement by vernadite (from Mn-feroxyhyte to Fe-vernadite), while

**Table 3.** Chemical composition (wt %) of (1–6) mutabilites and (7) pseudobrookite from soils and oxykerchenite (8–11) from floodplain alluvium of the Vychegda River

| Component                      | 1      | 2     | 3     | 4     | 5     | 6     | 7     | 8     | 9     | 10    | 11    |
|--------------------------------|--------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| SiO <sub>2</sub>               | 56.03  | 44.18 | 45.19 | 47.57 | 7.48  | 22.54 | 3.64  | 6.89  | 0.65  | 1.48  | 1.66  |
| TiO <sub>2</sub>               | 0.48   | –     | 0.69  | 0.61  | –     | 0.55  | 19.03 | –     | –     | –     | –     |
| Al <sub>2</sub> O <sub>3</sub> | 24.71  | 5.07  | 20.78 | 29.99 | 2.85  | 10.6  | 1.61  | 3.63  | 0.81  | 0.68  | 0.62  |
| FeO                            | 11.15  | 23.72 | 18.21 | 8.82  | 30.22 | 6.98  | 72.24 | 28.12 | 33.46 | 30.58 | 38.77 |
| MnO                            | –      | –     | –     | –     | –     | –     | –     | 1.25  | 1.77  | 1.2   | 0.81  |
| CaO                            | 0.24   | 0.24  | –     | 0.18  | 0.27  | –     | –     | –     | –     | –     | –     |
| MgO                            | 4.43   | 1.32  | 4.38  | 4.13  | –     | 1.42  | 0.3   | 0.15  | –     | –     | –     |
| BaO                            | –      | 1.17  | –     | –     | 0.97  | –     | –     | –     | –     | –     | –     |
| K <sub>2</sub> O               | 3.87   | 0.41  | 2.67  | 6.04  | 0.42  | 2.44  | 0.41  | 0.14  | –     | –     | –     |
| P <sub>2</sub> O <sub>5</sub>  | 1.86   | 19.57 | 10.16 | –     | 10.18 | –     | 0.68  | 32.25 | 34.21 | 37.53 | 34.65 |
| Total                          | 100.82 | 95.64 | 102.4 | 97.84 | 53.54 | 45.3  | 100   | 72.64 | 71.09 | 80.6  | 76.6  |

Note: The analyses were performed with a JSM 6400 SEM equipped with a Link EDS and Microsped wave spectrometer. Analyst V.N. Fillipov.

- (1)  $(\text{Si}_{2.16}\text{Ti}_{0.01}\text{Al}_{1.12}\text{Fe}_{0.32}\text{Mg}_{0.24}\text{Ca}_{0.01}\text{K}_{0.19}\text{P}_{0.06})_{4.11}\text{O}_7 \cdot n\text{H}_2\text{O}$ ;  
 (2)  $(\text{Si}_{1.84}\text{Al}_{0.25}\text{Fe}_{0.74}\text{Mg}_{0.08}\text{Ca}_{0.01}\text{Ba}_{0.02}\text{K}_{0.02}\text{P}_{1.72})_{4.68}\text{O}_7 \cdot n\text{H}_2\text{O}$ ;  
 (3)  $(\text{Si}_{1.77}\text{Ti}_{0.02}\text{Al}_{0.1}\text{Fe}_{0.54}\text{Mg}_{0.26}\text{K}_{0.13}\text{P}_{0.33})_{4.01}\text{O}_7 \cdot n\text{H}_2\text{O}$ ;  
 (4)  $(\text{Si}_{1.93}\text{Ti}_{0.02}\text{Al}_{1.5}\text{Fe}_{0.28}\text{Mg}_{0.26}\text{Ca}_{0.01}\text{K}_{0.33})_{4.32}\text{O}_7 \cdot n\text{H}_2\text{O}$ ;  
 (5)  $\text{K}_{0.08}(\text{Fe}_{2.36}\text{Ca}_{0.04}\text{Ba}_{0.06})_{2.46}[\text{Si}_{1.13}\text{P}_{1.3}\text{Al}_{0.51}\text{Fe}_{1.06}\text{O}_{10}] \cdot 47\text{H}_2\text{O}$ ;  
 (6)  $\text{K}_{0.44}(\text{Fe}_{0.74}\text{Mg}_{0.3}\text{Ti}_{0.06}\text{Al}_{0.96})_{2.16}[\text{Si}_{3.19}\text{Al}_{0.81}\text{O}_{10}] \cdot 52\text{H}_2\text{O}$ ;  
 (7)  $\text{Fe}_2(\text{Ti}_{0.58}\text{Fe}_{0.22}\text{Si}_{0.15}\text{Al}_{0.08}\text{Mg}_{0.02}\text{K}_{0.02}\text{P}_{0.02})_{1.09} \cdot \text{O}_5$ ;  
 (8)  $(\text{Fe}_{3.72}\text{Al}_{0.75}\text{Mn}_{0.18}\text{Ca}_{0.03})_{4.68}[(\text{P}_{0.8}\text{Si}_{0.2})\text{O}_4]_6 \cdot 33\text{H}_2\text{O}$ ;  
 (9)  $(\text{Fe}_{5.1}\text{Al}_{0.18}\text{Mn}_{0.3})_{5.58}[(\text{P}_{0.98}\text{Si}_{0.02})\text{O}_4]_6 \cdot 39\text{H}_2\text{O}$ ;  
 (10)  $(\text{Fe}_{5.4}\text{Al}_{0.15}\text{Mn}_{0.27})_{5.82}[(\text{P}_{0.96}\text{Si}_{0.04})\text{O}_4]_6 \cdot 18\text{H}_2\text{O}$ ;  
 (11)  $(\text{Fe}_{5.64}\text{Al}_{0.15}\text{Mn}_{0.12})_{5.92}[(\text{P}_{0.94}\text{Si}_{0.06})\text{O}_4]_6 \cdot 30\text{H}_2\text{O}$ .

the second group corresponds to vernadite dominated by alkaline-earth and alkaline elements rather than Fe.

Based on the microprobe analysis, the empirical formulas of indicated mineral series are as follows:

- (1)  $(\text{Fe}_{0.38-0.66}\text{Mn}_{0.33-0.57}\text{Ca}_{0-0.04}\text{Ba}_{0-0.01}\text{K}_{0-0.01})\text{OOH} \cdot n\text{H}_2\text{O}$ ;  
 (2)  $(0.8-0.95)\text{MnO}_2[(0.01-0.09)\text{Fe}_2\text{O}_3(0.02-0.11)\text{CaO}(0-0.05)\text{MgO}(0-0.01)\text{BaO}(0-0.02)\text{Na}_2\text{O}(0-0.02)\text{K}_2\text{O}] \cdot n\text{H}_2\text{O}$ .

In thin sections, the development of manganese hydroxides after iron hydroxides is rarely observed as a phase process. More commonly, it occurs as “degeneration” of feroxyhyte with a change of its color from orange-brown to black owing to increasing Fe loss and proportional Mn enrichment ( $r = -0.87$ ). The gradual transition from iron oxides into manganese hydroxides is presumably provided by the diffusive replacement of Fe by Mn.

Chemically, the oxide mineralization in the considered alluvial sands is a typical ferromanganese mineralization (Table 2). The manganese content in it is com-

pletely controlled by dioxide content ( $r = 0.99$ ). Therefore, in terms of some important parameters ( $\text{Mn}/\text{Fe} = 1.56$ ,  $\text{MnO}_2/\text{Mn} > 1.2$ ), the studied mineralization approximates the economic-grade ores. This explains a significant enrichment of the low-grade fluvial mineralization by manganese hydroxides (Chernov, 1944).

#### GENETIC HYPOTHESIS

The carried out investigations indicate that Mn-rich alluvium is distinctly confined to so-called “deflected” shores, where steep bendings of river floodplain cause

**Table 4.** Chemical composition of manganese and ferromanganese oxyhydroxides from alluvial sand of the Vychehga and Sysola rivers

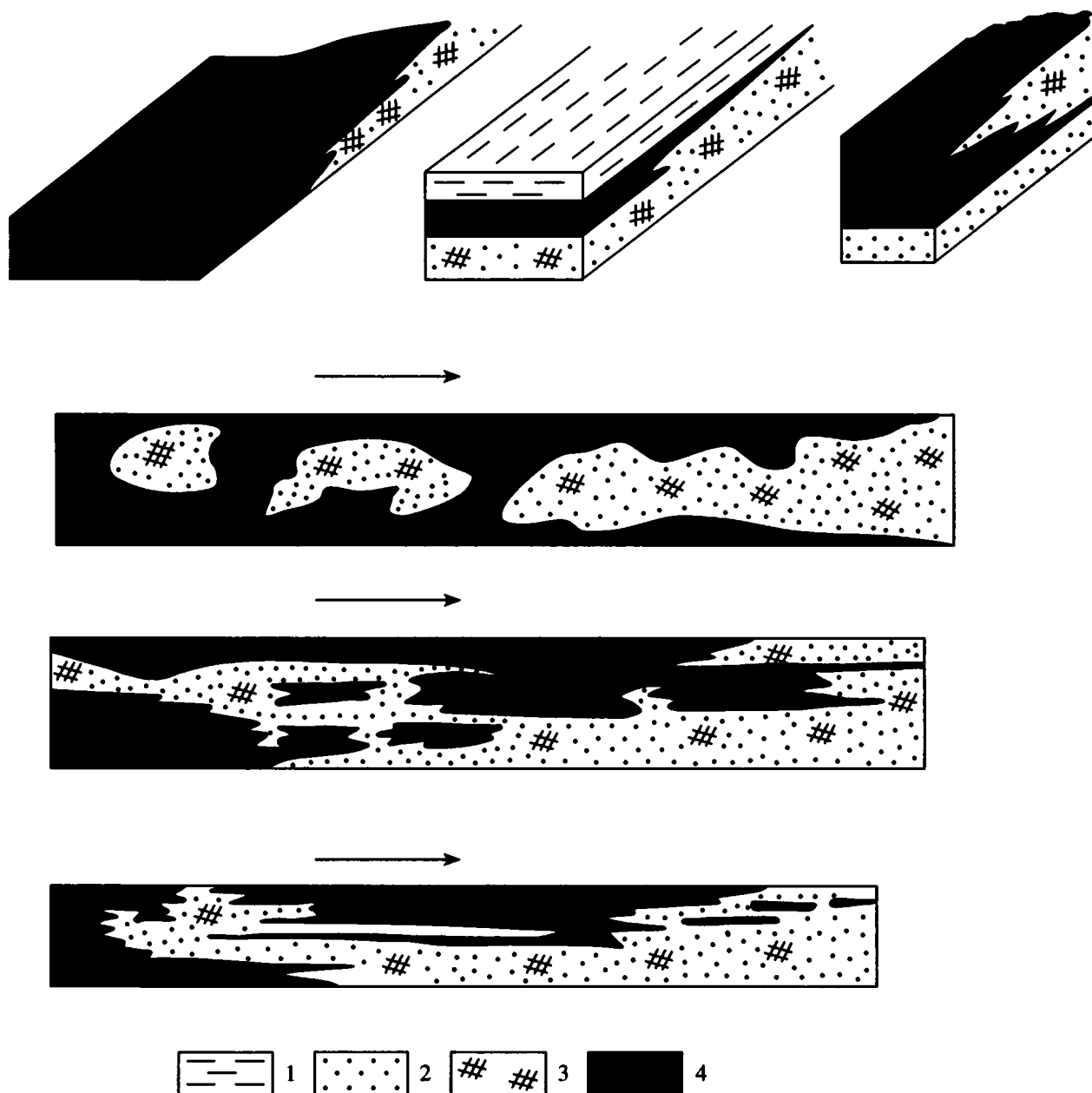
| Component                      | Oxyhydroxides |       |       |       |       |       |       |       |       |       |       |       |       |       |
|--------------------------------|---------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
|                                | Manganese     |       |       |       |       |       |       |       |       |       |       |       |       |       |
|                                | 1             | 2     | 3     | 4     | 5     | 6     | 7     | 8     | 9     | 10    | 11    | 12    | 13    | 14    |
| SiO <sub>2</sub>               | 22.20         | 22.89 | 24.18 | 10.80 | 0.19  | 0.11  | 2.40  | 13.02 | 4.31  | 4.49  | 2.04  | 10.66 | 0.73  | 3.11  |
| TiO <sub>2</sub>               | 0.19          | 0.31  | 0.20  | 1.43  | 1.53  | 2.59  | 1.87  | 0.09  | 0.05  | 0.02  | —     | 0.12  | —     | —     |
| Al <sub>2</sub> O <sub>3</sub> | 9.16          | 7.83  | 9.77  | 3.98  | 0.01  | —     | 1.02  | 5.29  | 2.02  | 1.72  | 0.77  | 4.01  | 0.46  | 1.19  |
| FeO                            | 4.09          | 4.49  | 4.45  | 1.91  | 0.12  | 0.15  | 0.60  | 1.86  | 1.20  | 0.90  | 0.29  | 1.90  | 0.14  | 0.44  |
| MnO                            | 42.90         | 43.58 | 40.19 | 64.11 | 80.75 | 79.93 | 76.00 | 50.87 | 62.56 | 55.26 | 61.02 | 46.71 | 62.02 | 62.02 |
| CoO                            | —             | —     | —     | —     | —     | —     | —     | —     | —     | —     | —     | —     | —     | —     |
| NiO                            | 0.10          | 0.09  | 0.06  | —     | —     | —     | —     | 0.01  | 0.06  | —     | 0.12  | 0.08  | —     | —     |
| CaO                            | 3.66          | 3.27  | 3.06  | 1.43  | 1.53  | 2.59  | 1.87  | 3.94  | 0.79  | 3.03  | 2.97  | 2.52  | 6.00  | 2.93  |
| MgO                            | 1.41          | 1.17  | 1.16  | 0.72  | 0.18  | 0.25  | 0.30  | 0.79  | 0.64  | 0.45  | 0.25  | 0.67  | —     | —     |
| BaO                            | —             | —     | —     | —     | —     | —     | —     | —     | —     | —     | —     | —     | —     | —     |
| Na <sub>2</sub> O              | 0.31          | 0.28  | 1.07  | 0.19  | 0.11  | 0.20  | 0.17  | 0.36  | 0.33  | 0.66  | 0.92  | 0.54  | —     | —     |
| K <sub>2</sub> O               | 0.91          | 0.84  | 0.91  | 0.61  | 0.47  | 0.35  | 0.47  | 1.90  | 0.54  | 0.53  | 0.33  | 0.58  | 0.45  | 1.04  |
| P <sub>2</sub> O <sub>5</sub>  | —             | —     | —     | —     | —     | —     | —     | —     | —     | —     | —     | —     | —     | —     |
| Total                          | 84.93         | 84.72 | 85.06 | 88.86 | 83.36 | 88.57 | 82.84 | 78.12 | 77.08 | 67.05 | 68.70 | 67.79 | 70.19 | 71.25 |

| Component                      | Oxyhydroxides |       |       |       |       |       |       |       |       |       |                |       |       |       |
|--------------------------------|---------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|----------------|-------|-------|-------|
|                                | Manganese     |       |       |       |       |       |       |       |       |       | Ferromanganese |       |       |       |
|                                | 15            | 16    | 17    | 18    | 19    | 20    | 21    | 22    | 23    | 24    | 25             | 26    | 27    | 28    |
| SiO <sub>2</sub>               | 0.90          | 6.51  | 11.27 | 3.68  | 14.14 | 8.74  | 7.58  | 9.12  | 4.77  | 1.40  | 7.92           | 4.44  | 5.51  | 0.02  |
| TiO <sub>2</sub>               | —             | —     | —     | —     | —     | —     | —     | —     | —     | —     | —              | 0.38  | —     | —     |
| Al <sub>2</sub> O <sub>3</sub> | 1.86          | 5.63  | 5.86  | 1.96  | 5.83  | 1.05  | 6.41  | 1.75  | 5.99  | 0.45  | 4.88           | 2.83  | 1.93  | —     |
| FeO                            | 0.25          | 1.46  | 1.12  | 0.62  | 9.22  | 5.06  | 2.19  | 0.53  | 2.82  | 0.76  | 26.04          | 27.69 | 23.99 | 61.80 |
| MnO                            | 61.77         | 58.05 | 51.83 | 62.03 | 41.57 | 47.25 | 51.30 | 53.62 | 52.07 | 58.27 | 34.23          | 34.40 | 36.35 | 30.80 |
| CoO                            | —             | —     | —     | —     | 2.92  | —     | —     | —     | —     | —     | —              | 2.33  | —     | —     |
| NiO                            | —             | —     | —     | —     | —     | —     | —     | —     | —     | —     | —              | —     | —     | —     |
| CaO                            | 4.61          | 5.24  | 4.60  | 4.54  | —     | 2.76  | 2.47  | 1.78  | 2.29  | 2.22  | 2.12           | —     | 2.19  | 0.12  |
| MgO                            | —             | 1.44  | 1.76  | —     | —     | —     | —     | —     | —     | —     | —              | —     | —     | 0.17  |
| BaO                            | —             | —     | —     | —     | 1.02  | 1.46  | 0.77  | 0.93  | 1.25  | 0.70  | 0.56           | 0.48  | 1.24  | —     |
| Na <sub>2</sub> O              | —             | —     | —     | —     | —     | —     | —     | —     | —     | —     | —              | —     | —     | 0.08  |
| K <sub>2</sub> O               | 0.20          | 0.26  | 0.42  | 0.23  | 0.45  | 0.21  | 0.28  | 0.49  | 0.36  | 0.48  | 0.31           | 0.39  | 0.20  | 0.01  |
| P <sub>2</sub> O <sub>5</sub>  | —             | —     | —     | —     | —     | —     | —     | —     | —     | —     | 1.29           | 1.12  | 1.53  | —     |
| Total                          | 70.77         | 81.09 | 78.47 | 74.34 | 75.21 | 67.04 | 71.39 | 68.38 | 69.90 | 64.74 | 77.54          | 74.29 | 73.34 | 93.01 |

the intense circulation (inflow–outflow) of water (Lukashev and Lukashev, 1972). It is noteworthy that the location of Mn-rich alluvium practically coincides with zones of drift wood accumulation in alluvial

deposits (Fig. 6). This explains the upstream and downstream thinning out of mineralization. Evidently, the mentioned fact is related with the change in hydrodynamic regime of river owing to riverbed straightening.



**Fig. 3.** Landward thinning out of mineralization. (1) Overlying loam, (2) underlying Fe-free sand, (3) iron hydroxide mineralization, (4) manganese hydroxide mineralization. The arrows show the direction of iron hydroxide replacement by manganese hydroxides.

The studied ferromanganese mineralization is distinctly confined to the most water-permeable horizons of continental deposits, through which the water percolates immediately into riverbeds. Our observations suggest that these horizons serve as a substrate that accumulates the ferromanganese hydroxides (Fig. 7).

The most important factor of manganese enrichment is a preliminary ferrugination of aquiferous sands, which was related with surface oxidation of Fe dissolved in groundwaters (Vakhtanova *et al.*, 1997). The development of manganese mineralization indicates that Mn in the considered conditions may be derived

only from river water. Therefore, the multi-level and irregular development of manganese mineralization in alluvial sands may be explained by seasonal fluctuations of water level and dissolved Mn content in the river water (Alekin and Brazhnikova, 1964; Kovalev *et al.*, 1974; Targul'yan, 1963). This mineralization type is also characterized by low (practically at the level of barren river sands) trace element (Co, Ni, Cu, Zn) contents.

The extremely low Mn content in river water discards the sedimentation as a direct mechanism of Mn accumulation in alluvial sands. In the considered con-



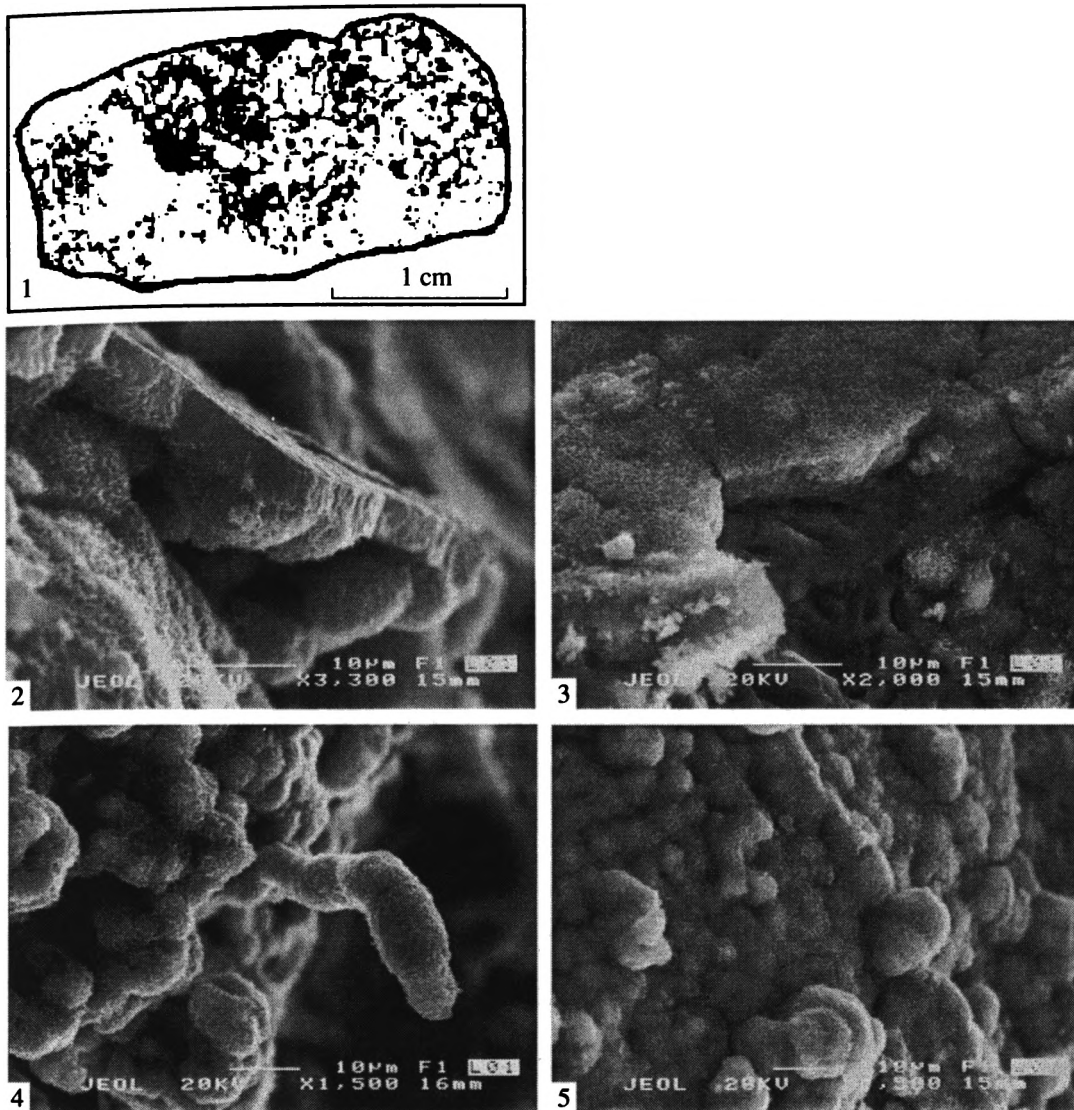
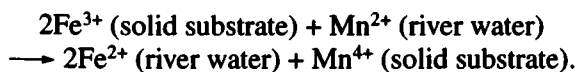


Fig. 4. (1) Cementation in mineralized alluvial sands, (2, 3) internal structure, and (4, 5) surface morphology of oxide crusts on terrigenous grains.

ditions, Mn may be accumulated only by the chemical adsorption of  $\text{Mn}^{2+}$  by active surfaces of iron hydroxides with the subsequent catalytic manganese oxidation during the following exchange redox reactions:



We suggest that this mechanism explains the Mn substitution for Fe in hydroxides. The appearance of first manganese hydroxide films on the accumulation surfaces autocatalytically accelerates the subsequent manganese oxidation.

It should be noted that such concepts were proposed (Volkov, 1977) and well justified for present-day oceanic, sea, and lacustrine ore formation (Bogdanov *et al.*, 1987; Chelishchev and Gribanova, 1983; Gold-

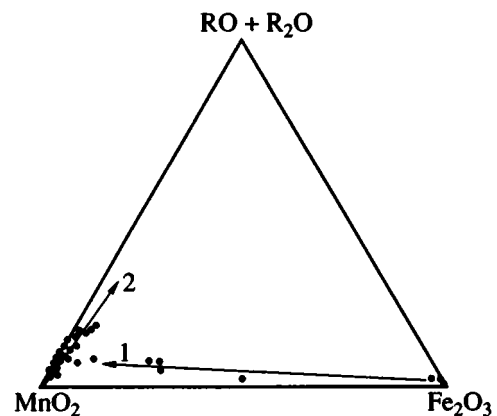
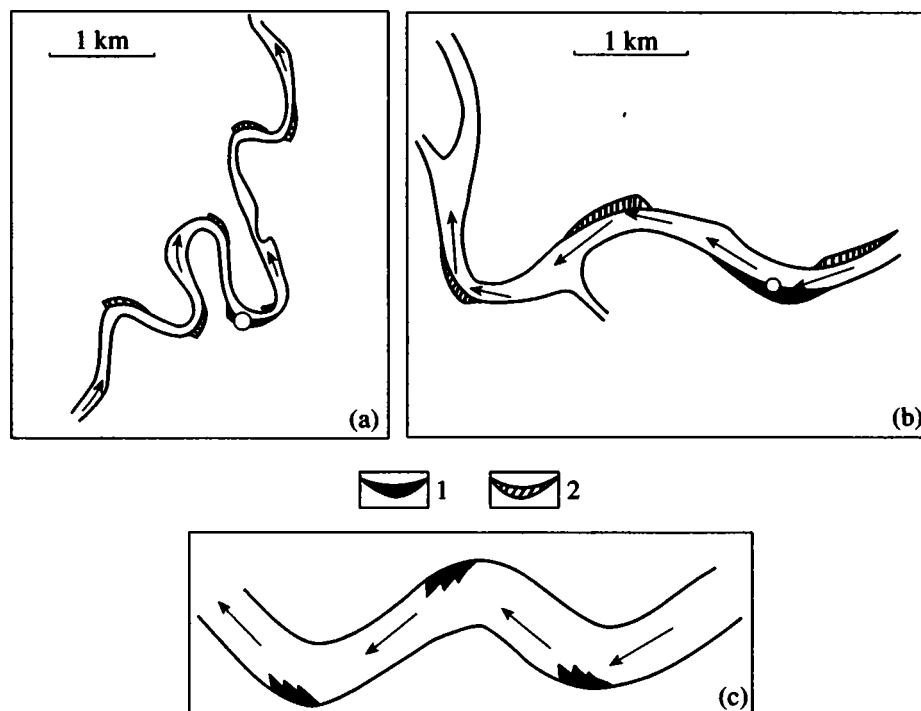
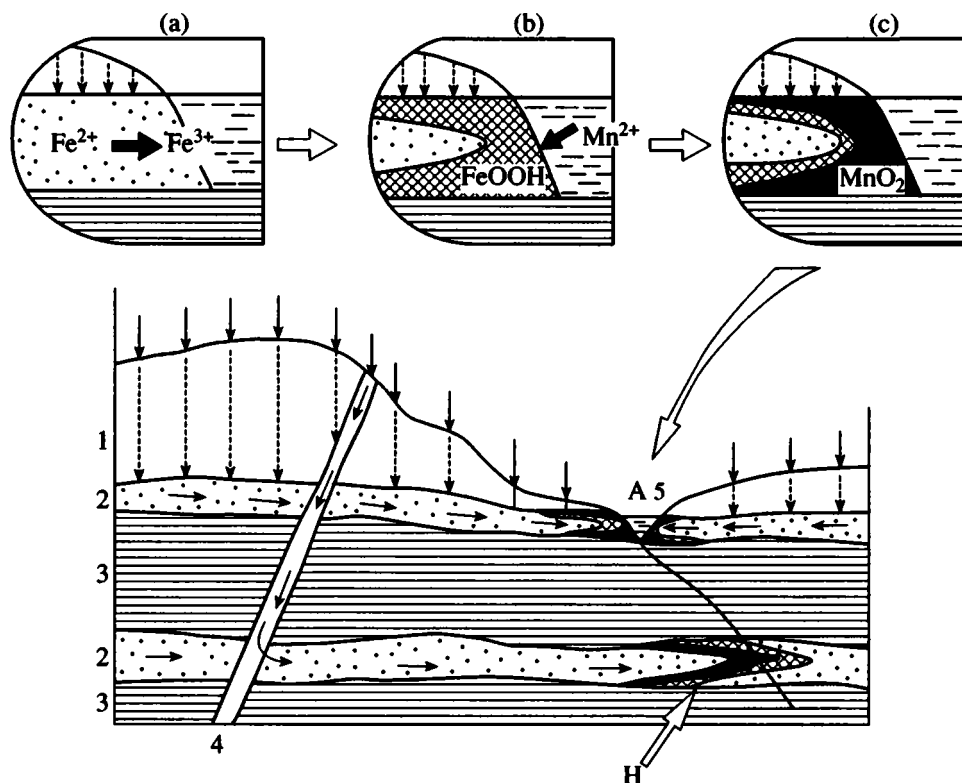


Fig. 5. Ternary diagram for aquagene ferromanganese hydroxides. Variations of mineral composition: (1) feroxyhyte-Fe-vernadite series; (2) vernadite.



**Fig. 6.** Location scheme of the aquagene manganese oxide mineralization at the (a) Sysola and (b) Vychegda rivers. (c) Scheme of drift wood accumulation in alluvium (Chemekov, 1951). (1) Studied and (2) inferred mineralized areas.



**Fig. 7.** Scheme of the (A) aquagene–river and (H) hydrogenous manganese oxide mineralization. (1) Infiltration zone, (2) aquiferous horizons, (3) aquiclude horizons, (4) disjunctive water conduits, (5) riverbed. The arrows show directions of stratal and transit water flows. (a–c) Sequence of oxide mineralization in the alluvial sand.

berg and Arrenius, 1958; Tikhomirov *et al.*, 1984; Varentsov, 1972; Varentsov *et al.*, 1990).

Based on the accepted Middle Holocene age of the Vychehda alluvium, the formation rate of manganese oxide cement may be estimated to be 0.15–0.5 mm/ka, which is 1–2 orders of magnitude more than the average growth rate of ferromanganese nodules and crusts in the pelagic areas of the present-day oceans (Timofeev *et al.*, 1976).

## CONCLUSIONS

The alluvial ferromanganese mineralization is formed within the most permeable ferruginous sand horizons, mainly in floodplain facies. The multi-level distribution of mineralization throughout the profile of sand-alluvial deposits is explained by its relation with individual aquiferous horizons, as well as by seasonal fluctuations of water level and  $Mn^{2+}$  content in river water. The manganese was accumulated from river water by the chemical sorption of  $Mn^{2+}$  on iron hydroxides with the subsequent oxidation during exchange redox processes.

Genetic properties of the studied alluvial mineralization indicate that it may be distinguished as an aquagene type of ferromanganese occurrences.

Aquagene ore occurrences are known not only in alluvial sands. The deposits of geyser, carst cave, and mine waters, reservoirs, technogenic settlers, and others are also ascribed to this type. We believe that the aquagene occurrences also include so-called nodules and crusts, which are widespread in recent lakes, seas, and oceans at the boundary between sediments and bottom water. The term "hydrogenous," which is commonly applied to ferromanganese nodules and crusts, is not correct, because it is taken from the geology of epigenetic intrastratal ore deposits.

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# Paleosols in Upper Permian Sedimentary Rocks, Sukhona River (Severnaya Dvina Basin)

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**Abstract**—Paleosols crop out in the Sukhona River valley as several members, up to 10 m thick, embedded into the Salarevo Formation sediments. Principal characteristics of paleosols include a dense network of root channels, indications of eluvial gley alteration, redistribution and formation of secondary carbonates represented by several generations, and formation of block-prismatic soil structure with specific clayey films at structural jointing faces. The paleosols are divided into a number of genetically interrelated horizons (from top to bottom): presumably organogenic accumulation (AEI<sub>g</sub>), eluvial gley horizon (EI<sub>g</sub>), illuvial horizons (B<sub>1</sub> and B<sub>2</sub>), illuvial gley horizon (Bg), and transitional horizons (EIB<sub>g</sub> and BEI<sub>g</sub>). Paleosols were formed under conditions of a semiarid climate with sharp seasonal or secular and multisecular oscillations of atmospheric precipitation. Such soils point to specific ecological environments, which were existing in the northern semiarid belt of the Earth before greatest (in the Phanerozoic) biospheric crisis at the Permian–Triassic boundary.

## INTRODUCTION

Paleosols<sup>1</sup> in Upper Tatarian sedimentary rocks of the Moscow Syncline were mentioned in literature for many times (Ignat'ev, 1963; Tverdokhlebov, 1996; Aref'ev and Naugol'nykh, 1998; Lozovskii and Esaulova, 1998). However, the detailed descriptions have been lacking despite a great scientific interest for soils of that age. Their study may provide additional information on climatic, sedimentational, and ecological environments of redstone and varicolored rock formation. In the late Permian, such rocks occupied vast territories at low and middle latitudes of the Earth (Zharkov and Chumakov, 1998). Late Tatarian environments attract particular interest, because they are related to the beginning of the Siberian glacier-free era,<sup>2</sup> when the long-term Gondwana glacial era gave way to the new warm state of biosphere. In addition, these environments provide insights into conditions, which were existing at the vast land before the greatest (in the Phanerozoic) biospheric crisis at the Permian–Triassic boundary.

Chalyshev (1968, 1974a, 1974b) made a significant contribution to the study of Permian and Triassic paleosols. His scientific results are mainly related to gray and

brown soils, as well as humid red soils, which sharply differ from arid and semiarid carbonate–gley red soils, which are subjects of our investigation.

In this communication, we report the results of field observations and laboratory studies of paleosols from one of the most complete Upper Tatarian sections exposed in the Sukhona River valley.

## RESEARCH OBJECTS AND METHODS

In the lower reaches of the Sukhona River, the paleosols occur in two upper (Poldarsa and Salarevo) formations of Upper Tatarian (Aref'ev and Naugol'nykh, 1998; Golubev, 1998). The lower Poldarsa Formation, about 80 m thick, mainly consists of gray (red in the middle part) calcareous clay and clayey siltstone with sparse interlayers of clayey limestone and marl, along with large lenses of oligomictic and quartz sandstones. The sediments were deposited in onshore shallow-water part of large lake, adjacent lowlands and, probably, deltas (Aref'ev and Naugol'nykh, 1998). Paleosol noticed in the Poldarsa Formation at several levels are thin and poorly developed.

The Salarevo Formation represents the Vyatka Horizon of the Upper Tatarian and has a thickness of 80–85 m. The formation almost completely consists of red and varicolored clayey siltstones and silty clay with a variable carbonate content, and polymictic sandstone. As in the Poldarsa Formation, the sandstone forms large lenses, occasionally deeply incised into underlying rocks. The marl and clayey limestone are much less

<sup>1</sup> The term *paleosol* is a synonym of terms *fossil soil* and *buried soil* (Glossary of Geology ..., 1972; Chetyrekh "yazychnyi entsiklopedicheskii ...", 1980, p. 317; Paleogeograficheskii slovar' ..., 1985, p. 189; Russko-angliiskii geologicheskii ..., 1998, p. 334).

<sup>2</sup> The Siberian glacier-free era, beginning in Tatarian and Late Tatarian, occupied the entire Mesozoic and terminated in Eocene (Chumakov, 1984). Sometimes, it is loosely called Mesozoic Era.

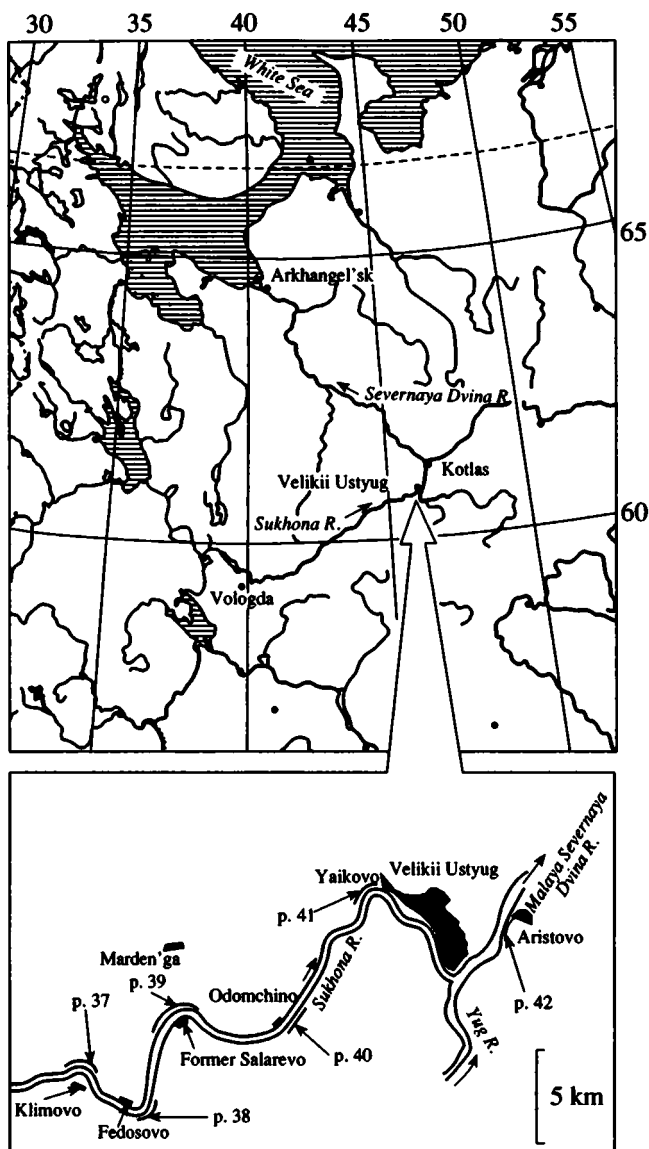


Fig. 1. Index map and section location.

abundant. The Salarevo Formation was deposited in the periodically flooded alluvial-proluvial and lacustrine plain (Ignat'ev, 1963; Aref'ev and Naugol'nykh, 1998) or, as some researchers assume, on the surface of a large delta (Tverdokhlebov, 1996). Sandy lenses of the Salarevo Formation are grouped at four stratigraphic levels and represent either the channel deposits of wandering rivers or deposits of delta branches (Aref'ev and Naugol'nykh, 1998). Numerous paleosol layers are especially abundant in the lower part of the Salarevo Formation within the so-called Rovda Member (Golubev, 1998), where such layers completely occupy some intervals of the section. Paleosols of the Rovda Member commonly overlap the sandy lenses and spread far beyond their limits.

We examined both formations in the lower reaches of the Sukhona River and described in more detail the paleosols of the Rovda Member in the Salarevo Formation. They were investigated in two bank outcrops near the Klimovo and Salarevo villages, which are separated by 6 km and well correlated (Fig. 1). The paleosol series occupying the middle part of exposures stands out by a variegated appearance. Paleosols occur between the upper, key limestone layer and the lower, large sandstone lense. Paleosols may be subdivided into two members (Fig. 2, members II and III; Fig. 3a). The thickness of the upper member is ~ 5.5 m; the lower member is 4 m thick. Both members are similar in composition and structure, but the lower member is distinguished by a markedly higher carbonate content. Each member consists of 4–5 paleosol layers immediately overlying each other (Fig. 2).

Each soil layer was comprehensively studied with respect to its texture and structure both in outcrops and in undistorted oriented specimens under a binocular microscope. Thin sections of paleosol were also examined under a petrographic microscope. Most representative profiles were characterized by the grain size distribution and chemical analyses, pH determinations of water extracts, determinations of organic carbon, and nonsilicate iron modifications (Mehr-Jackson extract). The < 0.005 mm fraction was analyzed with the XRD method, while the 0.05–0.01 mm fraction was a subject of mineralogical analysis.

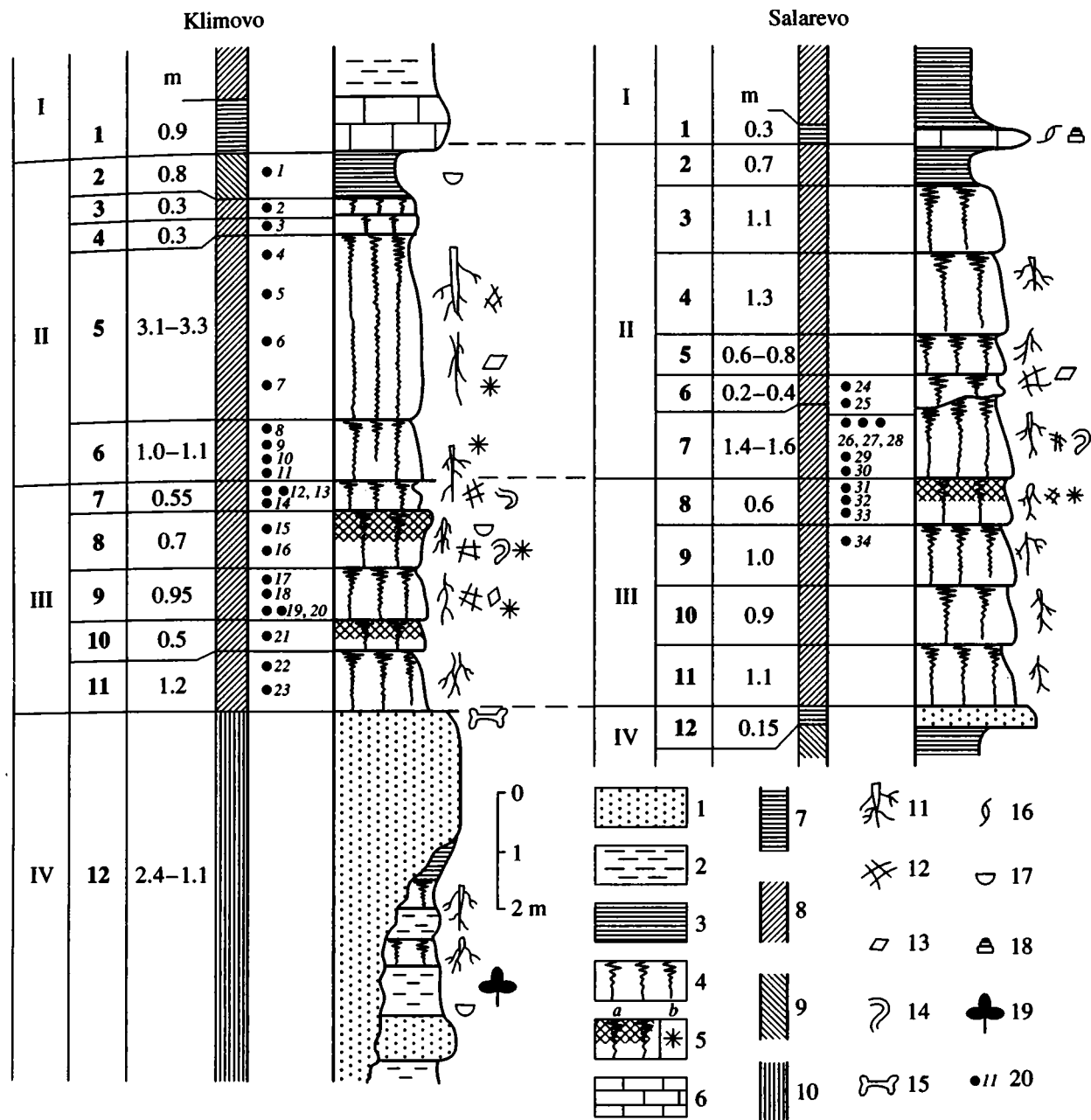
## CHARACTERISTICS OF PALEOSOLS

Paleosols are rather uniform in grain size. The silty clay is prevalent, while the highly clayey siltstone is subordinate. The total sum of psammitic and coarse silty fractions is commonly below 1%. Their content is approximately 2% in three samples and reaches 9.7% only in one sample (Table 1). The grain size spectrum reveals a distinct and stable bimodality with maxima related to fine silty, clayey, and subcolloidal fractions. The 0.05–0.01 mm fraction is mainly represented by quartz, feldspar, and muscovite grains with an admixture of pyroxene, epidote, and occasional amphibole (Fig. 4). Analcime is present in virtually all samples.

According to 25 XRD determinations, the clayey fraction (< 0.005 mm) of paleosols is fairly uniform and mainly consists of smectite group minerals (Fig. 5). Hydromica and chlorite contents are below 5–6%; analcime is abundant.

In contrast to uniform grain size and mineral composition, the texture and color of paleosols are extremely diverse. The detailed study allowed us to recognize the horizons similar to genetic horizons of modern soils. The multifold alternation of eluvial and illuvial horizons indicates the occurrence of several soil profiles formed by *in situ* paleosol-forming processes. The various intensity of eluvial and illuvial<sup>3</sup> processes

<sup>3</sup> In the soil science, illuvial process designates the delivery of dissolved matter or suspension from the overlying soil horizon.



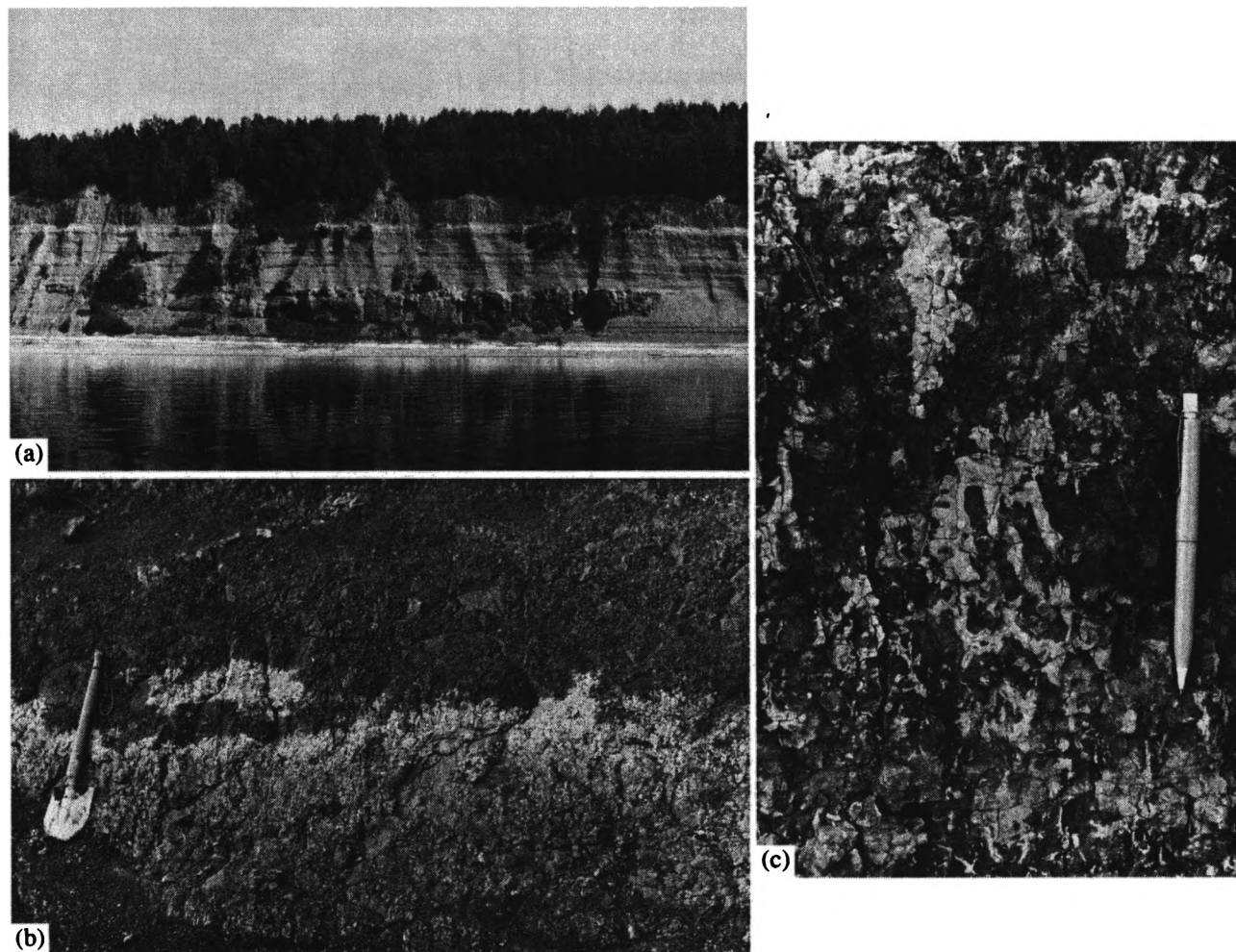
**Fig. 2.** Paleosol sections in the lower part of the Salarevo Formation, Upper Tatarian Substage in the lower reaches of the Sukhona River (Rovda Member). Rocks: (1) sandstone, (2) siltstone, (3) clay; paleosols: (4) low-carbonate, (5a) high-carbonate, (5b) with carbonate nodules; (6) limestone; rock color: (7) gray, (8) varicolored, (9) red, (10) light brown; paleosol structure: (11) relics of root systems, (12) multiorder block and prismatic soil jointing, (13) stress and sliding cutans (small slickensides on clay surfaces); (14) clay sinters (illuviation cutans), organic remains: (15) tetrapoda, (16) bivalves, (17) ostracoda, (18) gastropoda; (19) megascopic plant remnants; (20) sample location and their number. (I–IV) member numbers; (1–12) layer and soil profile numbers.

ses in combination with variable duration of soil-forming stage and sedimentation rate provided a variety of soil profiles. Most typical of them are shown in Fig. 6. As a rule, they consist of 2–4 genetic horizons. Horizons of eluvial gley alteration are denoted in the figure by Elg; the illuvial gley horizons, by Bg; illuvial horizons without indications of gleying, by B<sub>1</sub> and B<sub>2</sub>; tran-

sitional horizons, by ElBg or BElg; and the slightly altered, soil-forming bedrock horizon, by BC–C.

In addition, the horizons, which are transitional from organogenic accumulative to eluvial gley, were established in two profiles (Klimovo exposure, profile 6, sample 8 and Salarevo exposure, profile 6, sample 24). They are denoted as AElg?. In the Salarevo Formation,





**Fig. 3.** Paleosols in deposits of the Upper Tatarian Substage, the Sukhona River. (a) General view of the Klimovo exposure (point 37); the sandstone lense (dark) is seen in the lower part of exposure and the rocks of Poldarsa Formation at its base; (b) typical paleosol profile (Klimovo exposure, member II, profile 8); the bleached soil horizon (Elg) is gradually replaced by underlying varicolored horizon (BElg); (c) a detail of ElBg soil horizon—gley tongues along root channels deeply penetrate the red-colored groundmass of the horizon.

this horizon overlies the bleached zone of the Bg horizon (Fig. 6, layer 6). Its thickness is 2–3 cm; the layer locally pinches out along the strike. Its lower boundary is gradual, and the soil texture is granular and obscure platy. The dark gray, clayey–silty AEIg? horizon is virtually carbonate-free. In contrast to other horizons where the mean organic carbon content is about 0.2% (Table 2), this horizon contains 0.6%  $C_{org}$ . The brownish gray clay in layer 6 (the Klimovo exposure) occupies a similar position in the soil profile, although its appearance differs from the above-mentioned layer. The lack of organic accumulative horizons in most profiles may be interpreted in various ways. They might have been mineralized during the postpedogenic diagenesis or eroded before the burial. However, it cannot be ruled out that the organogenic accumulative horizons were not formed in the Permian at all due to the

absence of turfy grass. The further study is required to clarify this problem.

Our work aimed at determining the position of AEIg and Elg horizons, which are situated closest to the paleosurface, was based on relatively sharp upper boundaries and the structure of root systems. The latter represent a three-dimensional network of branching and downward thinning channels filled with clay or two generations of calcite. The channels are surrounded by gley haloes. The diameter of axial root channels of the first order varies from 4 to 10 mm, the second-order offsets have a diameter of 2–4 mm, and the third-order offsets, 0.5–1.0 mm. The length of axial channels commonly exceeds 10 cm. In some cases, the mineralized remains and imprints of roots with a plant microtexture are retained; several morphological types and two new root species have been reported (Aref'ev and Naugol'nykh, 1998). The spacing and diameter of root

**Table 1.** Grain size of paleosols from the Salarevo Formation

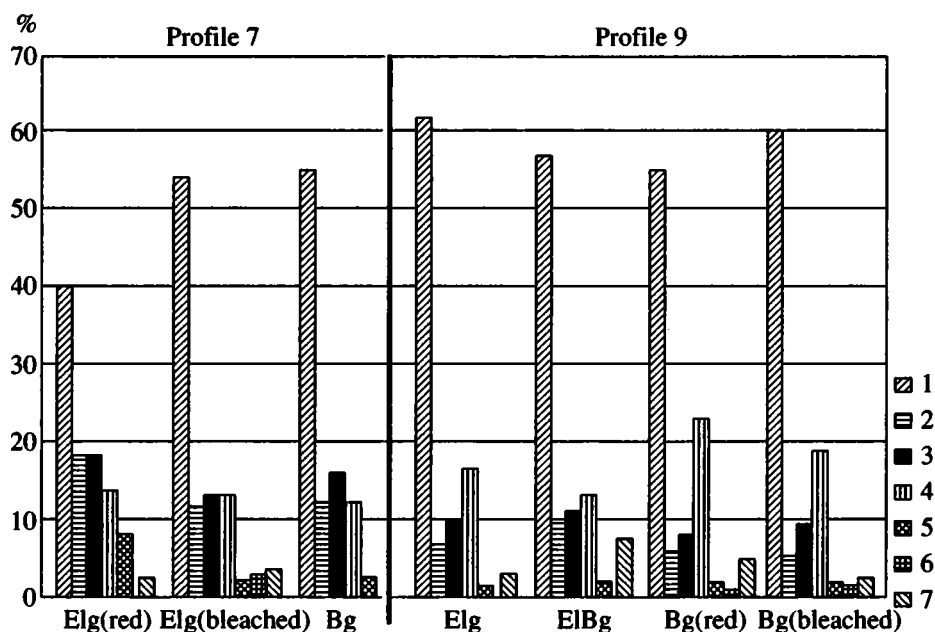
Table 1

| Member   | Layer | Horizon              | Thickness,<br>cm | Fraction, mm |           |           |            |             |        |
|----------|-------|----------------------|------------------|--------------|-----------|-----------|------------|-------------|--------|
|          |       |                      |                  | 1-0.25       | 0.25-0.05 | 0.05-0.01 | 0.01-0.005 | 0.005-0.001 | <0.001 |
| Klimovo  |       |                      |                  |              |           |           |            |             |        |
| III      | 7     | Elg (red)            | 15-20            | 0.00         | 0.02      | 36.89     | 13.70      | 27.22       | 22.17  |
|          |       | (bleached)           |                  | 0.01         | 0.04      | 53.09     | 10.93      | 18.75       | 17.18  |
|          | 7     | Belg                 | 30-35            | 0.08         | 2.20      | 36.10     | 17.16      | 18.93       | 25.53  |
|          | 8     | ElBg                 | 20-30            | 0.05         | 0.85      | 57.55     | 11.22      | 9.37        | 20.96  |
|          | 8     | BElg                 | 45-50            | 0.09         | 2.33      | 44.43     | 11.91      | 18.49       | 22.75  |
|          | 9     | ElBg                 | 10-15            | 0.04         | 9.63      | 37.61     | 10.82      | 22.46       | 19.34  |
|          | 9     | B <sub>1</sub> g     | 20-25            | 0.36         | 0.56      | 42.43     | 10.64      | 25.74       | 20.27  |
|          | 9     | B <sub>2</sub> (red) | 55-60            | 0.02         | 0.02      | 9.4       | 23.94      | 33.49       | 32.95  |
|          |       | (bleached)           |                  | 0.02         | 2.01      | 39.42     | 12.93      | 23.72       | 22.20  |
| Salarevo |       |                      |                  |              |           |           |            |             |        |
| II       | 6     | AElg?                | 12-15            | 0.06         | 0.28      | 23.59     | 11.24      | 33.54       | 31.29  |
|          | 6     | Bg                   | 20-25            | 4.28         | 0.03      | 22.35     | 8.05       | 30.59       | 38.93  |
|          | 7     | ElBg (red)           | 35-45            | 0.01         | 0.04      | 36.25     | 18.0       | 8.14        | 37.56  |
|          |       | (bleached)           |                  | 0.02         | 0.02      | 29.53     | 11.10      | 30.12       | 29.21  |
|          |       | (mixed)              |                  | 0.14         | 0.24      | 22.24     | 11.16      | 29.26       | 36.96  |
|          | 7     | B <sub>1</sub> g     | 40-45            | 0.04         | 0.05      | 10.90     | 11.62      | 40.68       | 36.71  |
|          | 7     | B <sub>2</sub>       | 67-70            | 0.02         | 0.01      | 1.89      | 16.21      | 25.55       | 56.32  |

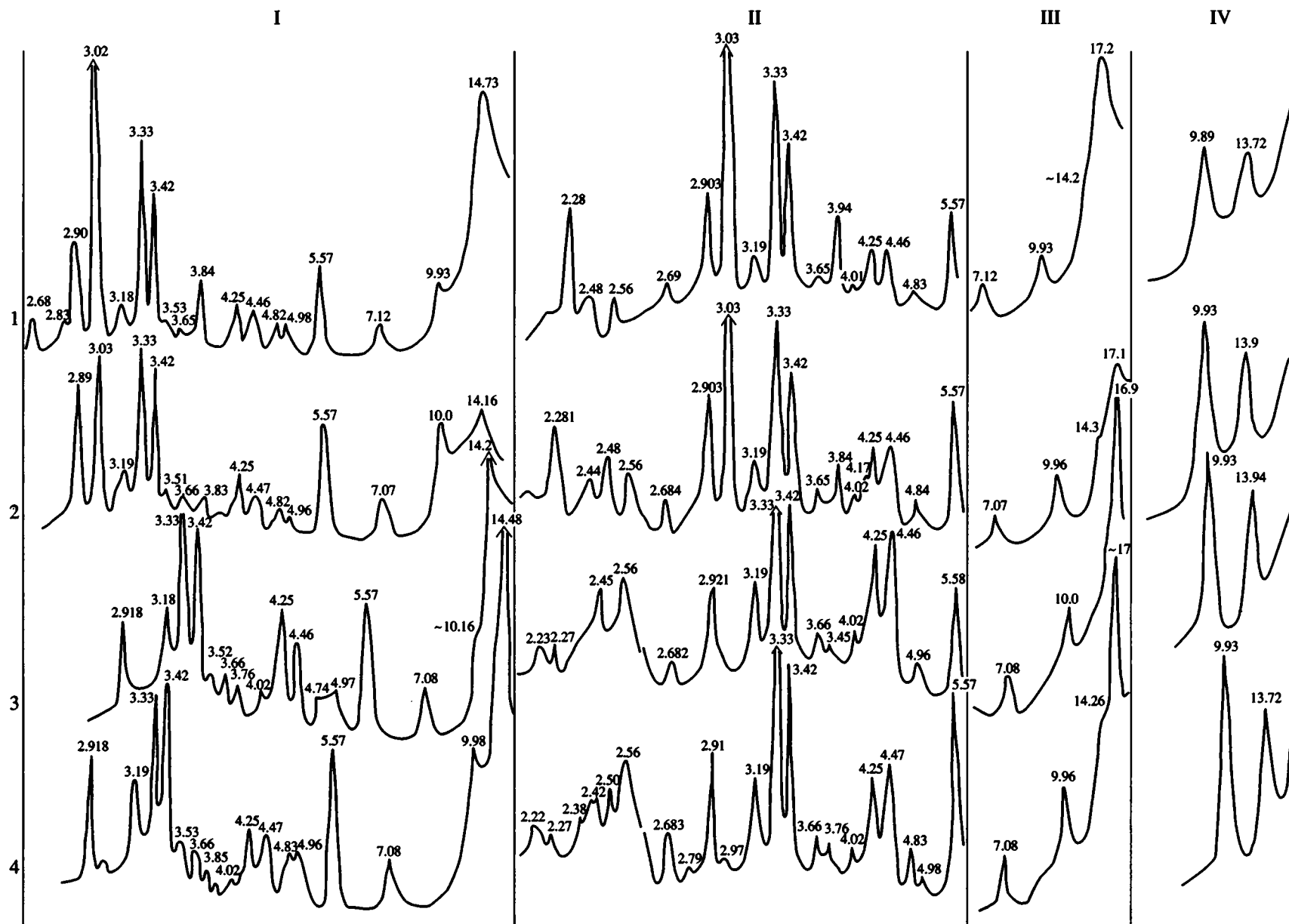
Note: Fraction contents are recalculated for the 100% volatile- and carbonate-free composition.

channels decrease from Elg to B horizon. The branching of root channels is accompanied by the decrease in their diameter and the change of orientation. In the

absence of compaction-related deformation, the straight root segments are commonly observed between the branching points. In general, the root systems reveal



**Fig. 4.** Mineral composition of the 0.05-0.01 mm fraction in soil horizons from profiles 7 and 9, the Salarevo Formation, Klimovo exposure. (1) Quartz; (2) K-feldspar, (3) plagioclase, (4) muscovite, (5) epidote, (6) amphibole and pyroxene, (7) analcime.



**Fig. 5.** Typical X-ray patterns of clay fraction (<0.005 mm) of paleosol horizons, Klimovo. (1) Elg (red); (2) Elg (bleached); (3) ElBg; (4) Bg. (I) Natural, (II) saturated with ethylene glycol, (III) calcinated at 550°C; (IV) powder.

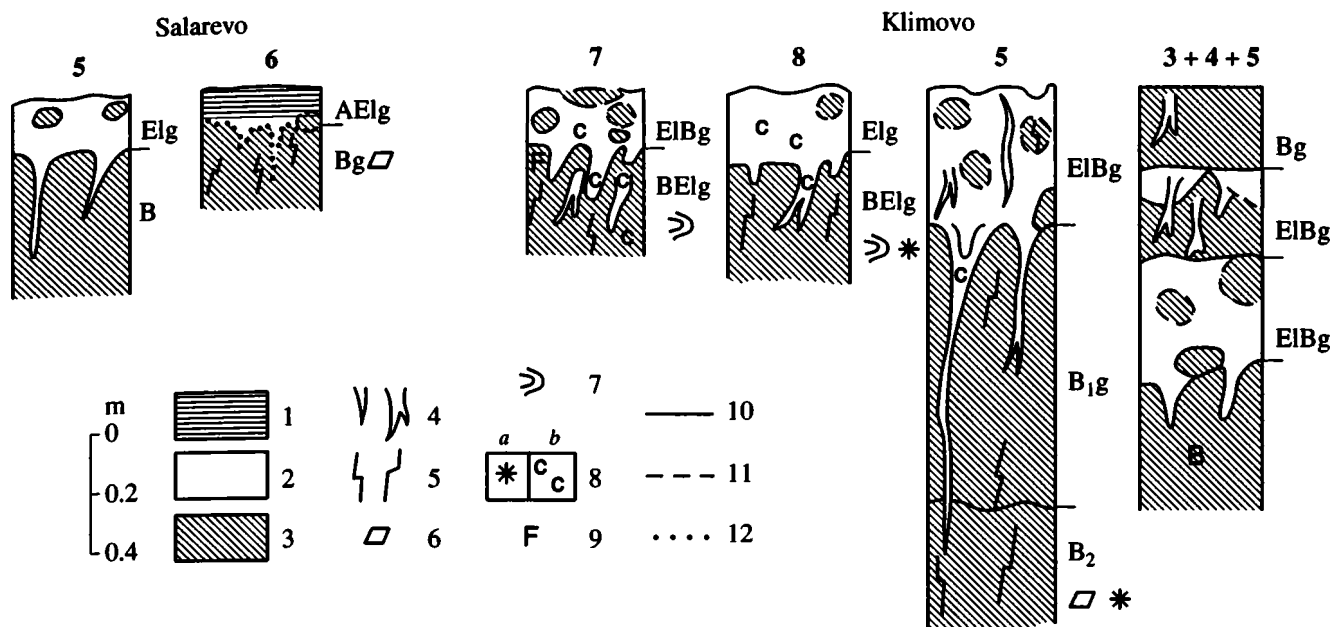


Fig. 6. Typical paleosol profiles in the Salarevo Formation (profile numbers correspond to Fig. 2). Soil horizons: AElg, Elg, ElBg, BElg, Bg, B, B<sub>1g</sub>, B<sub>2</sub>. Horizon color: (1) gray, (2) whitish blue, (3) reddish brown; structures: (4) root channel, (5) multiorder block structure, (6) sliding cutans, (7) clayey illuvated cutans; (8a) carbonate nodules; (8b) elevated carbonate content; (9) ferrugination zones; horizon boundaries: (10) clearly expressed, (11) gradual, (12) very gradual.

a hierarchical fractal structure. The nearly vertical extension and branching of root channels, their deep penetration without a sharp reorientation of root systems, indicate the absence of aquifers or low-permeable layers (Retallack, 1990). Relics of root system are one of most typical features of the soils under study.

The extensive development of root remains in Upper Tatarian sediments along the Sukhona River was noticed by many researchers who studied in detail the Vyatka Horizon (Ignat'ev, 1963; A. Minikh and M. Minikh, 1981; Strok *et al.*, 1984; Strok, 1987; Tverdokhlebov, 1996; Golubev, 1998; Aref'ev and Naugol'nykh, 1998). Root remains at the same stratigraphic level are known elsewhere at the Russian Plate (Lozovskii and Blom, 1998; Tverdokhlebov, 1998) and are regarded as a typical feature of the Vyatka Horizon (Ignat'ev, 1963, 1998; Strok *et al.*, 1984). Concerning the recent investigations of the Vyatka Horizon at the Sukhona River, only Verzhilin *et al.* (1993) did not point out the root relics. Being adherents of the concept of deep lagoon genesis, they referred the root channels as mudeater or worm trails. However, such interpretation is not consistent with the above-described features of root systems, in particular, with the thinning of branching root channels, the rectilinear character of channels of the first and second orders between branching points, and their general fractal structure.

In most paleosols, the following three successively replacing genetic horizons represent typical profiles (from the top to bottom). The eluvial gley (Elg) horizon is commonly 10–30 cm thick. This is the most bleached

horizon, whitish in a dry state and grayish blue in a wet state (Fig. 3b). The root channels, which are discerned within the light material, are filled with a still paler, almost white matter. Isolated rounded and angular spots of pale brown, reddish and red color—the remnants of gleyed bedrock—are incorporated into the bleached mass (Fig. 6, Klimovo, profile 8). The Elg horizon is composed of the clayey siltstone with a various carbonate content. Depending locally on carbonate contribution, the rock varies in strength from brittle to rather hard state. The platy and block jointing denoted in pedology as a soil structure is characteristic of this horizon.

As can be seen under a microscope, the most fine-grained (< 0.005 mm) material is represented by a clayey carbonate, clayey-ferruginous or clayey plasma<sup>4</sup> of low birefringence. The silty and fine sandy fractions are mainly represented by angular grains of quartz, feldspars, and muscovite with an admixture of epidote, analcime, less abundant calcite, amphibole, and pyroxene. In some cases, the clastic grains are accumulated in pores, which commonly remains empty. The pore walls are uneven and devoid of newly formed linings. The lower boundary of the Elg horizon is rough: deep nearly vertical branching tubular haloes of whitish gray mineral extend along root systems and deeply penetrate the underlying redstone of the ElBg horizon.

<sup>4</sup> In the soil science, the finely dispersed and most labile material involved into the soil-forming process is named *plasma*.

**Table 2.** Some chemical properties of paleosols from the Salarevo Formation, %

| Member | Layer | Horizon                   | Thickness, cm | pH (H <sub>2</sub> O) | C <sub>org</sub> | Fe <sub>2</sub> O <sub>3</sub> , nonsilicate |
|--------|-------|---------------------------|---------------|-----------------------|------------------|----------------------------------------------|
| II     | 2     | Climovo                   |               |                       |                  |                                              |
|        | 3     | C                         | 70–80         | 8.6                   | –                | 3.65                                         |
|        | 4     | BC                        | 20–30         | 8.75                  | –                | 3.90                                         |
|        | 4     | EIBg                      | 20–30         | 8.7                   | –                | 3.10                                         |
|        | 4     | EIBg                      | 20–30         | 8.4                   | –                | 1.49                                         |
|        | 5     | EIBg                      | 40–50         | 9.2                   | –                | 2.38                                         |
|        | 5     | B <sub>1</sub> g (upper)  | 120–130       | 9.3                   | –                | 2.77                                         |
|        | 5     | B <sub>1</sub> g (middle) | 120–130       | 8.55                  | –                | 2.96                                         |
|        | 5     | B <sub>1</sub> g (lower)  | 120–130       | 8.05                  | –                | 3.26                                         |
|        | 5     | B <sub>2</sub> (red)      | 140–150       | 8.4                   | –                | 3.26                                         |
|        | 5     | B <sub>2</sub> (bleached) | 140–150       | 9.5                   | –                | 1.12                                         |
|        | 6     | AElg                      | 10–12         | 8.8                   | –                | 2.74                                         |
|        | 6     | EIBg                      | 25–30         | 8.2                   | –                | 3.00                                         |
|        | 6     | Bg                        | 35–40         | 8.3                   | –                | 3.21                                         |
| III    | 7     | Elg (red)                 | 15–20         | 8.3                   | 0.19             | 2.56                                         |
|        | 7     | Elg (bleached)            | –             | 8.45                  | 0.13             | 0.28                                         |
|        | 7     | BEIg                      | 30–35         | 7.9                   | 0.07             | 3.37                                         |
|        | 8     | EIBg                      | 20–30         | 8.3                   | 0.15             | 2.48                                         |
|        | 8     | BEIg                      | 45–50         | 8.4                   | 0.18             | 3.62                                         |
|        | 9     | EIBg                      | 10–15         | 8.2                   | 0.23             | 2.75                                         |
|        | 9     | B <sub>1</sub> g          | 20–25         | 8.5                   | 0.27             | 3.48                                         |
|        | 9     | B <sub>2</sub> (red)      | 55–60         | 8.3                   | 0.16             | 3.87                                         |
|        | 9     | B <sub>2</sub> (bleached) | –             | 8.5                   | 0.14             | 0.27                                         |
|        | 10    | EIBg                      | 45–50         | 7.8                   | –                | 2.06                                         |
| II     | 11    | Elg                       | 25–30         | 7.5                   | –                | 1.51                                         |
|        | 11    | BC                        | 80–90         | 8.4                   | –                | 3.73                                         |
|        |       | Salarevo                  |               |                       |                  |                                              |
|        | 6     | AElg?                     | 12–15         | 8.6                   | 0.60             | 2.24                                         |
|        | 6     | Bg                        | 20–25         | 8.4                   | 0.03             | 3.65                                         |
|        | 7     | EIBg (red)                | 35–45         | 8.5                   | 0.02             | 1.67                                         |
|        | 7     | EIBg (bleached)           | 35–45         | 8.6                   | 0.15             | 0.19                                         |
|        | 7     | EIBg (mixed)              | 35–45         | 8.5                   | 0.05             | 1.39                                         |
|        | 7     | B <sub>1</sub> g          | 40–45         | 8.4                   | 0.32             | 3.91                                         |
| II     | 7     | B <sub>2</sub>            | 65–70         | 8.6                   | –                | 3.84                                         |
|        | 8     | Elg (upper)               | 25–30         | 9.4                   | –                | 0.39                                         |
|        | 8     | Elg (lower)               | 25–30         | 9.85                  | –                | 1.30                                         |
|        | 8     | BEIg                      | 30–35         | 9.95                  | –                | 2.15                                         |
|        | 9     | BEIg                      | 50–55         | 8.9                   | –                | 1.72                                         |

Note: Dash denotes "not determined."

The eluvial–illuvial (EIBg) horizon commonly varies in thickness from 30 to 60 cm. It stands out by the brightest and mottled color with a combination of vertical bleached eluvial zones and the prevalent partly illuviated red bedrock (Fig. 6, Klimovo exposure, profile 7); the multiorder equant and prismatic soil structure (jointing) is observed. Bleached root tubes, from 1–3 to 3–15 mm in diameter, are composed of decolorized gley material (Fig. 3c). At the periphery, the root channels are filled with secondary fine-crystalline dirty calcite while the coarse-crystalline pure calcite fills the axial zones of channels. The host red-brown material is represented by a limonitized clayey–silty mass, which is more intensely ferruginated along the fractures. Severely ferruginated spots are also scattered throughout this mass. Under a microscope, the ferruginated clay material and secondary carbonates are seen close to pores. The alternation of carbonate and ferruginous zones testifies to their polychronous and likely multifold formation. Bleached gley tubes near roots penetrate into underlying horizons to depths ranging from 30–80 to 100–150 cm. In some cases, the tubes penetrate the upper bleached horizon of the underlying paleosol. Sinter clayey films (cutans) and signs of compression and sliding (stress cutans) are observed at joint surfaces within the red clay material. Small spindle-shaped clayey carbonate nodules, up to 1 × 2 mm in size, are occasionally noticed in the EIBg horizon. The BEIg horizon, 30–40 cm thick, bears a transitional character. It differs from the above-described EIBg horizon by a lesser area of whitish blue near-root zones and hence by a prevalence of red sediment over the whitish blue material (Fig. 6, Klimovo exposure, profile 7).

The illuvial–gley (Bg) horizon is commonly 40–65 cm thick (up to 1 m) and is distinguished by substantially clayey composition and more monotonous red color. When the blue tint is almost absent, the horizon is denoted by a symbol B. The illuvial horizon is subdivided into B<sub>1</sub> and B<sub>2</sub> subhorizons with different soil structure, density, color and other features. Isolated narrow, whitish blue spots of near-root zones penetrating from above are still discernible in the Bg horizon. As a rule, Bg, B<sub>1</sub>, and B<sub>2</sub> horizons are most compact. The multiorder prismatic and block soil structure with disintegrated angular fragments is well expressed. Axial parts of root tubes are filled with a virtually pure secondary calcite. Thin root channels enter soil aggregates of low orders. Thin cutans and stress cutans are seen on joint faces. Elongated, irregular, and often larger (2 × 5 mm) clayey–carbonate nodules are more abundant in the Bg horizon than in the EIBg horizon; small (0.5–1.0 mm) carbonate spots are also noticed. As can be seen under a microscope, these horizons consist of very fine material and are depleted in silty clastic grains. The material is enriched in optically oriented clay, which occurs in the groundmass and occasionally appears near pores. Some pores are filled with anal-

Table 3. Chemical compositions of paleosols

| Member | Layer | Horizon                   | Thick-<br>ness, cm | L.O.I. | CO <sub>2</sub> | SiO <sub>2</sub> | TiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | FeO  | MnO  | CaO   | MgO   | Na <sub>2</sub> O | K <sub>2</sub> O | P <sub>2</sub> O <sub>5</sub> |
|--------|-------|---------------------------|--------------------|--------|-----------------|------------------|------------------|--------------------------------|--------------------------------|------|------|-------|-------|-------------------|------------------|-------------------------------|
| II     | 2     | C                         | 70–80              | 19.7   | 10.25           | 51.91            | 0.65             | 14.87                          | 8.12                           | 0.32 | 0.22 | 12.45 | 7.63  | 2.45              | 1.79             | 0.15                          |
|        | 3     | BC                        | 20–30              | 12.45  | 2.7             | 59.29            | 0.87             | 16.5                           | 9.67                           | 0.47 | 0.09 | 5.98  | 3.05  | 2.49              | 1.95             | 0.17                          |
|        | 4     | ElBg                      | 20–30              | 10.47  | 1.65            | 63.98            | 0.7              | 16.26                          | 6.25                           | 0.26 | 0.04 | 4.59  | 3.8   | 2.83              | 1.82             | 0.11                          |
|        | 5     | ElBg                      | 40–50              | 7.43   | 0.35            | 68.37            | 0.67             | 14.52                          | 5.12                           | 0.16 | 0.02 | 2.75  | 2.56  | 3.24              | 1.75             | 0.14                          |
|        | 5     | B <sub>1</sub> g (upper)  | 120–130            | 9.1    | 0.75            | 64.65            | 0.72             | 14.77                          | 7.8                            | 0.23 | 0.02 | 3.16  | 3.87  | 2.2               | 2.27             | 0.21                          |
|        | 5     | B <sub>1</sub> g (lower)  | 120–130            | 9.12   | 1               | 62.17            | 0.7              | 16.48                          | 8.34                           | 0.13 | 0.02 | 2.94  | 3.79  | 2.72              | 2.05             | 0.2                           |
|        | 5     | B <sub>2</sub>            | 140–150            | 11.78  | 1.35            | 60.64            | 0.75             | 17.56                          | 8.4                            | 0.23 | 0.06 | 4.43  | 4.14  | 1.8               | 2.34             | 0.08                          |
|        | 6     | AEIlg?                    | 10–12              | 12.6   | 0.35            | 61.92            | 0.73             | 18.6                           | 6                              | 0.21 | 0.05 | 3.1   | 3.61  | 2                 | 2.7              | 0.18                          |
|        | 6     | ElBg                      | 25–30              | 11.8   | 0.45            | 62.01            | 0.77             | 18.27                          | 7.94                           | 0.17 | 0.06 | 2.86  | 3.38  | 1.83              | 2.55             | 0.12                          |
|        | 6     | Bg                        | 35–40              | 11.19  | 0.65            | 62.07            | 0.78             | 19.18                          | 7.48                           | 0.17 | 0.03 | 2.53  | 3.39  | 2.35              | 2.51             | 0.16                          |
|        | 6     | BC                        | 20–30              | 8.12   | 0.2             | 65.71            | 0.79             | 15.97                          | 5.82                           | 0.34 | 0.01 | 3.18  | 2.62  | 2.05              | 3.23             | 0.23                          |
| III    | 7     | Elg (red)                 | 15–20              | 11.21  | 3.85            | 61.97            | 0.82             | 14.92                          | 7.52                           | 0.43 | 0.06 | 7.57  | 1.97  | 1.63              | 2.77             | 0.17                          |
|        | 7     | Elg (bleached)            | 15–20              | 15.75  | 6.25            | 58.28            | 0.84             | 12.5                           | 4.55                           | 0.5  | 0.09 | 15.54 | 2.93  | 1.91              | 2.64             | 0.18                          |
|        | 7     | BEIlg                     | 30–35              | 13.13  | 3.3             | 59.35            | 0.85             | 13.36                          | 7.61                           | 0.51 | 0.21 | 9.74  | 3.82  | 1.52              | 2.82             | 0.18                          |
|        | 8     | ElBg                      | 20–30              | 33.66  | 32.75           | 22.7             | 0.48             | 5.54                           | 3.88                           | 0.44 | 0.38 | 62.53 | 1.75  | 1.27              | 0.89             | 0.11                          |
|        | 8     | BEIlg                     | 45–50              | 20.68  | 15.95           | 49.36            | 0.71             | 11.02                          | 6.01                           | 0.4  | 0.13 | 23.13 | 5.33  | 1.71              | 1.99             | 0.18                          |
|        | 9     | ElBg                      | 10–15              | 22.38  | 18.05           | 46.31            | 0.73             | 10.06                          | 6.49                           | 0.57 | 0.26 | 27.31 | 4.77  | 1.3               | 2.16             | 0.11                          |
|        | 9     | B <sub>1</sub> g          | 20–25              | 14.41  | 7.9             | 57.61            | 0.91             | 12.67                          | 7.05                           | 0.43 | 0.09 | 11.99 | 4.64  | 1.9               | 2.36             | 0.2                           |
|        | 9     | B <sub>2</sub> (red)      | 55–60              | 21.65  | 13.35           | 46.37            | 0.69             | 13.5                           | 8.76                           | 0.37 | 0.41 | 19.37 | 6.64  | 1.68              | 1.75             | 0.1                           |
|        | 9     | B <sub>2</sub> (bleached) | 55–60              | 16.28  | 10.55           | 57.35            | 0.75             | 13.84                          | 4.67                           | 0.3  | 0.16 | 14.24 | 4.13  | 2.11              | 2.11             | 0.23                          |
|        | 10    | ELBg                      | 45–50              | 23.3   | 17.99           | 45.39            | 0.51             | 12.42                          | 7.62                           | 0.4  | 0.43 | 17.34 | 11.82 | 1.93              | 1.65             | 0.18                          |
| II     | 11    | Elg                       | 25–30              | 9.69   | 0.3             | 62.11            | 0.72             | 17.88                          | 6.62                           | 0.5  | 0.03 | 2.68  | 4.11  | 2.62              | 2.48             | 0.18                          |
|        | 11    | BC                        | 80–90              | 21.31  | 15.85           | 48.96            | 0.53             | 11.46                          | 5.64                           | 0.4  | 0.41 | 18.82 | 9.42  | 2.03              | 2.06             | 0.2                           |
|        |       | Salarevo                  |                    |        |                 |                  |                  |                                |                                |      |      |       |       |                   |                  |                               |
|        | 6     | AEIlg?                    | 12–15              | 10.31  | 0.75            | 63.86            | 0.87             | 18.53                          | 5.79                           | 0.4  | 0.02 | 2.03  | 3.84  | 1.3               | 2.58             | 0.23                          |
|        | 6     | Bg                        | 20–25              | 12.75  | 2.3             | 62.61            | 0.76             | 16.99                          | 6.74                           | 0.54 | 0.05 | 4.51  | 3.58  | 1.19              | 2.77             | 0.23                          |
|        | 7     | ElBg                      | 35–45              | 10.9   | 2.2             | 64.03            | 0.77             | 17.21                          | 3.94                           | 0.48 | 0.04 | 4.73  | 3.05  | 1.9               | 3.08             | 0.55                          |
|        | 7     | B <sub>1</sub> g          | 40–45              | 17.87  | 9.2             | 53.39            | 0.73             | 14.92                          | 8.26                           | 0.44 | 0.13 | 13.48 | 4.3   | 1.02              | 2.7              | 0.12                          |
|        | 7     | B <sub>2</sub>            | 65–70              | 13.66  | 3.45            | 57.91            | 0.8              | 15.86                          | 10.4                           | 0.42 | 0.08 | 6.17  | 3.86  | 1.11              | 2.97             | 0.19                          |
|        | 8     | Elg (upper)               | 25–30              | 25.48  | 21.75           | 40.35            | 0.62             | 10.61                          | 3.19                           | 0.46 | 0.2  | 38.53 | 2.42  | 2.42              | 1.34             | 0.21                          |
|        | 8     | Elg (lower)               | 25–30              | 22.06  | 16.85           | 48.63            | 0.72             | 10.18                          | 3.81                           | 0.64 | 0.18 | 27.74 | 4.6   | 1.35              | 1.99             | 0.14                          |
|        | 8     | BEIlg                     | 30–35              | 21.89  | 16.7            | 47.44            | 0.69             | 11.15                          | 4.67                           | 0.5  | 0.25 | 25.89 | 5.98  | 1.11              | 2.15             | 0.15                          |
|        | 9     | ElBg                      | 50–55              | 27.09  | 19.4            | 45.79            | 0.78             | 10.29                          | 3.95                           | 0.5  | 0.31 | 28.16 | 6.59  | 1.15              | 2.33             | 0.14                          |

Note: All compositions (wt %) are recalculated for the 100% volatile-free composition.

The BC horizon is a very compact red clayey rock without visible indications of pedogenesis except sparse and thin root channels filled with a bleached material.

Thus, both sections are characterized by a multifold intercalation of soil profiles consisting of regular sequences of soil horizons with a various degree of red bedrock alteration. Virtually unaltered or slightly

**Table 4.** Chemical composition of carbonates in paleosols of the Salarevo Formation, wt %

| Member | Layer | Horizon                   | Thickness, cm | IR    | R <sub>2</sub> O <sub>3</sub> | CaO  | MgO  | CO <sub>2</sub> | Total | CaCO <sub>3</sub> | CaMg(CO <sub>3</sub> ) <sub>2</sub> | Excess                 |
|--------|-------|---------------------------|---------------|-------|-------------------------------|------|------|-----------------|-------|-------------------|-------------------------------------|------------------------|
| II     | 2     | Klimovo                   |               |       |                               |      |      |                 |       |                   |                                     |                        |
|        |       | C                         | 70–80         | 62.67 | 4.56                          | 9.52 | 2.99 | 10.25           | 89.99 | 10.67             | 11.65                               | MgO, 0.44              |
| III    | 8     | ElBg                      | 20–30         | 21.55 | 1.37                          | 41.8 | <0.1 | 32.75           | 97.47 | 74.47             | –                                   | CaO, 0.08              |
|        | 8     | BEIg                      | 45–50         | 56.64 | 2.4                           | 17.7 | 0.51 | 15.7            | 92.9  | 30.23             | 2.34                                | CO <sub>2</sub> , 1.29 |
|        | 9     | ElBg                      | 10–15         | 52.42 | 2.27                          | 20.1 | 0.76 | 18.05           | 93.62 | 34.02             | 3.48                                | CO <sub>2</sub> , 1.43 |
|        | 9     | B <sub>1</sub> g          | 20–25         | 70.54 | 3.21                          | 9.71 | <0.1 | 7.9             | 91.36 | 17.33             | –                                   | CO <sub>2</sub> , 0.28 |
|        | 9     | B <sub>2</sub> (red)      | 55–60         | 55.82 | 3.02                          | 14.9 | 1.83 | 13.35           | 89.45 | 22.95             | 6.82                                | MgO, 0.34              |
|        | 9     | B <sub>2</sub> (bleached) | 55–60         | 66.17 | 3.45                          | 11.8 | 0.71 | 10.55           | 92.64 | 19.29             | 3.24                                | CO <sub>2</sub> , 0.52 |
|        | 10    | ElBg                      | 45–50         | 52.3  | 3.32                          | 12.8 | 5.62 | 17.99           | 92.06 | 8.94              | 25.71                               | CO <sub>2</sub> , 1.75 |
| II     | 11    | BC                        | 80–90         | 54.77 | 2.91                          | 13.3 | 5.28 | 15.85           | 92.15 | 11.56             | 22.56                               | MgO, 0.35              |
|        |       | Salarevo                  |               |       |                               |      |      |                 |       |                   |                                     |                        |
|        | 7     | B <sub>1</sub> g          | 40–45         | 67.2  | 3.27                          | 11.2 | 0.85 | 9.2             | 91.7  | 19.01             | 1.75                                | MgO, 0.47              |
|        | 8     | Elg (upper)               | 25–30 (upper) | 42.09 | 2.9                           | 27.4 | <0.1 | 21.75           | 94.17 | 48.96             | –                                   | CO <sub>2</sub> , 0.22 |
| III    | 8     | Elg (lower)               | 25–30 (lower) | 53.85 | 1.81                          | 20.4 | 0.34 | 16.85           | 93.23 | 35.54             | 1.55                                | CO <sub>2</sub> , 0.51 |
|        | 8     | BEIg                      | 30–35         | 55.02 | 1.54                          | 20.2 | 0.44 | 16.7            | 93.86 | 34.9              | 1.99                                | CO <sub>2</sub> , 0.51 |

Note: IR is insoluble residue.

altered basal B<sub>2</sub> and BC horizons are gradually replaced by severely altered illuvial Bg, B<sub>1</sub>, BEIg horizons and then by eluvial ElBg and Elg horizons. This indicates that the alteration was related to a pulsational introduction of the parental substance rather than secondary processes, which simultaneously affected the entire body of rocks. The relatively fast deposition of red, nonlayered clayey siltstone of various thickness was followed by a long-term period of soil formation. Judging by a development of B horizon, the soil formation lasted for hundreds and thousands of years (Retallack, 1990).

In general, the substrate and paleosols are rather uniform. Although the paleosols are represented by sets of similar horizons, they differ from each other in thickness and degree of development. This points to a general similarity of sedimentation and soil formation conditions in combination with various duration of cycles or insignificant climatic fluctuations. The occurrence of immature paleosol profiles may be a result of (1) periodical denudation of the surface horizons, (2) short-term hiatuses insufficient for a vigorous bedrock alteration, and (3) specific combination of contemporaneous pedogenesis and sedimentation when the bedrock was altered not only downward but also upward as commonly takes place in the loess.

The paleosols under study reveal a markedly various degree of carbonatization. The upper paleosol member is depleted in carbonates. The highest CO<sub>2</sub> content reaches only 2.7% whereas the CO<sub>2</sub> content in the lower member is as much as 20–35% or even 74% in some cases (Tables 3, 4). The carbonate is commonly represented by low-magnesian calcite. The limy dolomite occurs at the base of lower paleosol member (Table 4, layers 10 and 11). The morphological features and color of paleosols remain the same regardless of the carbonate content. The varicolored appearance of ElBg, BEIg, and Bg is determined by a redistribution of iron oxides rather than a carbonate content (Table 2). Bleached zones are not always enriched in carbonate while redstones are not always depleted. The paleosol structure also slightly depends on the carbonate content. In combination with a strict stratigraphic position of carbonate-rich soils, this implies that the carbonate content in paleosols is mainly determined by a carbonate content in the soil-underlying bedrock. This statement is supported by findings of ostracods in carbonate-rich paleosols; these fossils are characteristic of basins with a carbonate sedimentation (Molostovskaya, 1981) and presumably basins with a variable or elevated salinity (Kukhtinov, 1998). In addition, it was



noticed that the amount of ostracods in paleosol may decrease with diminishing of carbonate content.

Three calcite generations (primary sedimentary, dirty fine-crystalline on walls of root tubes, and pure coarse-crystalline) indicate the multistage mineral formation. It is not excluded that a part of crystalline carbonate was formed during and after the pedogenesis, e.g., as a result of  $\text{CaCO}_3$  gain by a surface water. The formation of carbonate nodules mainly in ElBg and Bg horizons was likely related to illuvial processes caused by a periodical atmospheric precipitation. It also cannot be ruled out that the relative enrichment of Elg and ElBg horizons in carbonate resulted from the flooding by a carbonate-rich water or the ascent of carbonates from deeper horizons along with capillary water and their subsequent precipitation near the surface.

The determination of pH as one of most labile parameters remains conventional in the case of such old soils. Nevertheless, it is interesting to note that, regardless of carbonate content, the pH value did not fall below 7.9 commonly remaining at 8.3–8.6 (Table 2). It may be inferred that the elevated pH was also typical of soil formation. This is confirmed by an occurrence of analcime, which often fills the pores in soil groundmass. This mineral, which is likely pedogenic in origin, serves as an indicator of the soil salinization (Retallack, 1990) or, at least, of the alkaline environment at one of soil formation stages (Travnikova *et al.*, 1973; Gorbunov and Bobrovitskii, 1973). The presence of analcime in paleosols also indicates the weathering of silicates. This is consistent with a disappearance of amphibole and pyroxene in the 0.01–0.05 mm fraction from some eluvial horizons whereas these minerals occur in underlying illuvial horizons (Fig. 4).

The total Fe distribution is in the full agreement with our version of soil profile structure. The total Fe content decreases in upper bleached horizons and increases in less gleyed redstone (Table 3). The comparison of bleached and redstone materials within one horizon support the enrichment of red matrix in the total Fe. It is evident that the variation of total Fe content is related to the migration of mobile nonsilicate Fe during the gleying in surface paleosol horizons and in zones adjoining the root channels, which serve as conduits for pH-depleted water migration.

The distribution of total and nonsilicate Fe is well consistent with morphological patterns characterizing the relationships between the bleached gley horizons and gleyed vertical tubes within redstone matrix. The redstone remnants within bleached horizons and the development of vertical bleached zones within redstone horizons clearly indicate that these subtypes of soil mass were developed *in situ* as a result of eluvial gley reworking of red bedrock. This suggestion is in agreement with the preservation of root systems in their lifetime position and the general grain-size similarity of whitish and red-colored materials. The relative amount

of principal fractions and their bimodal distribution remain the same in all horizons.

Besides the fractionation of nonsilicate Fe, the bleached material of the Elg horizon and bleached zones of ElBg and Bg horizons are markedly depleted in clay material and respectively enriched in silty material in comparison with underlying redstone or redstone remnants within bleached horizons. Such redistribution may be interpreted as a suspension transfer of fine clay material both within one layer and from one layer to another. This is supported by a formation of thin cutans on joint walls. This process operates only under a periodically arising excess in moisture followed by a subsequent drainage.

### GENETIC INDICATIONS OF PALEOSOLS

The above-described profiles are referred to as paleosols on the basis of the following indications.

(1) The sequential combination of several genetic soil horizons within profiles.

(2) A more distinct upper boundary of most soil profiles and subprofiles as compared with intraprofile boundaries.

(3) The closely spaced root channels, which become more and more sparse and thin down the profile; such structure indicates that the soils were formed *in situ*.

(4) The clearly expressed eluvial gley alteration with a removal of nonsilicate Fe from clay, which becomes gray in color; the process also results in a partial loss of clay material and amphibole and pyroxene breakdown.

(5) The illuvial process giving rise to the enrichment of B horizon in nonsilicate Fe, clay, and carbonate nodules.

(6) The multiorder soil structure, i.e., the jointing system in soil horizons. The platy, block, and prismatic jointing is typical. The hierarchy of soil structure is most expressive in the B horizon and in redstone relics of the Elg horizon.

(7) The sinter clay films (cutans) on jointing planes indicating the clay transport within the soil profile under conditions of temporal wetting, and the slickensides commonly developed in soils due to frequent swelling and dessication of smectite mineral mass.

### CONCLUSIONS

In summary, the following statements may be formulated. In the late Tatarian, red-colored and variously carbonated silty clay (loam), marl, and limestone were deposited on the lacustrine-alluvial plain. At the present time, these sedimentary rocks are exposed in the Sukhona River valley. In the early Salarevo time, the carbonate-rich loam and marl were deposited mainly in lakes with a migrating coastline or in seasonal lakes. Somewhat later, the slightly carbonated loam was formed on the plain episodically flooded by

seasonal streams and wandering rivers and on the delta surfaces. During hiatuses, the soils were formed on lacustrine and flood deposits and modified their primary appearance. Most important soil-forming processes included: (1) elluvial gley process (reduction and removal of iron oxides) manifested as a frontal reduction in upper horizons and local reduction along root systems; (2) migration and precipitation of carbonates indicating the arid environment of sedimentation and pedogenesis; (3) development of multiorder soil structures (hierarchy of soil jointing) related to the activity of root systems and periodical wetting and drying of various soil horizons; and (4) illuvial processes with a migration of solution and fine clay material from upper horizons of soil profile to the lower horizons.

Various combinations of such processes, variable duration of soil formation, different rates of sedimentation and diverse biota (Aref'ev and Naugol'nykh, 1998) resulted in a variety of soil profiles. Many of them fit the rather mature soil. The described soils are very specific and have no modern counterparts (Yakimenko *et al.*, 1998). Following the Russian–French terminology, more habitual in Russia, the soils under discussion should be defined as elluvial gley red fersialitic soils that can be subdivided into low- and high-carbonate varieties. In terms of the modern international classification presented in the World Reference Base for Soil Resources (WRB) (Deckers *et al.*, 1998), the soils should be named as gley-glossic chromic calcisols (low- and high-carbonate varieties). This definition is approximately deciphered as variously red-colored soils with gleyed layers, the lower boundary of which is tongue-shaped.

The close counterparts of paleosols under study were reported by Perel'man and Borisenko (1965, 1991) and Borisenko (1971, 1973, 1980) as paleopedogenic and epigenetic gley alteration of Paleozoic and Mesozoic carbonate redstones. The presence of carbonates and gley zones in redstones of the Cis-Urals region investigated by Perel'man and Borisenko brings them together with Upper Permian paleosols from the Sukhona River valley. However, the key point of the concept assuming the carbonate gley catagenesis of red-colored paleosols and rocks as an epigenetic alteration after the burial and subsequent stratal water circulation, advocated by Borisenko and Perel'man, hardly can be completely applied to the paleosols discussed in this paper. These soils do not reveal an eluvial–illuvial pedogenic redistribution of carbonates. The gley zones are not horizontally developed along the periphery of water-saturated layers, as was pointed out by Borisenko and Perel'man, but are nearly vertical and demonstrate a specific branching of gley zones along downward narrowing root channels of plants. In addition, the principal similarity of grain size distribution in soil horizons more likely testifies to the existence of aquiferous layers in bleached paleosol horizons described in this paper.

The paleosols under discussion were formed in subarid climate with sharp seasonal and secular (multisecular) fluctuations of atmospheric precipitation and respective hydrological conditions.

These conclusions support and substantially specify previous geological and paleontological data suggesting lacustrine–alluvial sedimentation environments and semiarid climate in the late Tatarian (Ignat'ev, 1963; Tverdokhlebov, 1996; Aref'ev and Naugol'nykh, 1998; and others). The inferred stable development of a relatively deep-water lagoonal basin (Verzilin *et al.*, 1993) is not confirmed. Abundant paleosols make an impressive case in favor of numerous and long (hundreds and thousands of years) hiatuses in sedimentation in the early Salarevo time. Hydromorphous soils clearly indicate the seasonal and more long-term episodic flooding of the region. Sharp seasonal fluctuations of humidity most likely should be regarded as remote manifestations of monsoon or even megamonsoon climate (Kutzbach and Callimore, 1989), which prevailed at the vast Pangea supercontinent. Permian monsoons might spread from the Paleotethys to the northwest into eastern Europe via plains, which occupied a wide territory between the West European Variscan mountain land and the Cis-Caucasus and Urals mountain chains. Attenuated monsoons might have reached the region under study.

Seasonal oscillations readily explain the ephemeroïd character of one group and the phreatophytic character of the second group of late Tatarian vegetation, which was existing in the Severnaya Dvina Basin (Aref'ev and Naugol'nykh, 1998). Secular and more long-term variations of precipitation were presumably caused by a periodical approaching of the moderate humid belt to the region, which was a part of the northern subarid climatic belt (Zharkov and Chumakov, 1998). As a result, polar fronts and cyclones invaded the territory.

It should be noted that Upper Permian red paleosols are widespread not only in many regions of eastern Europe (Ignat'ev, 1963; Feofilova, 1975; Tverdokhlebov, 1996) but are also abundant in western Europe where they are extensively developed from England to Bulgaria (Mader, 1992). Revealing some common features with Upper Permian red-colored paleosols of the Russian Platform, the post-Variscan soils in Europe bear many indications of their formation under variable sedimentation and climatic conditions in intramontane or proximal foredeep environments, as well as in coastal zones of Zechstein salt-bearing basins. Therefore, the paleosols of the Russian Platform, which were formed at vast plains, bear more information on climatic patterns of the Late Permian northern semiarid belt of Pangea.

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# Water Migration Coefficients of Chemical Elements in the Hypergenesis Zone

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**Abstract**—The contents of basic salt components in the continental discharge related to weathering processes were calculated taking into account the atmospheric transfer of soluble salts from the ocean and their supply from anthropogenic sources. Real water migration coefficients characterizing the mobility of chemical elements in the hypergenesis zone were calculated on the basis of these data. It has been shown that the water migration coefficient directly depends on the solubility of basic minerals that are stable in the hypergenesis zone.

In the theory of lithogenesis developed by Strakhov (1960), the mobilization of substance in drainage areas is considered as the initial stage of the process responsible for the formation of sedimentary rocks. During this process, the substance is separated into two sharply different (in migration mobility) classes: soluble salts and solid residual products of weathering. The differentiation determines in many respects specific features of the chemical composition of rocks that are formed in seas and oceans at the final stage of lithogenesis.

In analyzing the migration mobility of chemical elements in the hypergenesis zone since the first publication of Polynov (1934) devoted to this question, it has been usually presumed that rocks interact with pure water, not originally containing any dissolved substances. Hence, the ratio of element concentrations in the water-derived mineral residue and rock, i.e., the water migration coefficient, is a quantitative characteristic of the capability of this element to pass into the dissolved state (Perel'man, 1989). However, substantial amounts of dissolved substances in the river discharge are related to the atmospheric transfer of marine cyclic salts (Garrels and Makkenzi, 1974; Korzh, 1976; Savenko, 1982) and the supply from anthropogenic sources. Therefore, in calculating the water migration coefficients, it is necessary to deduct the contribution of cyclic salts and anthropogenic sources from the total amount of dissolved substances. The purpose of the present work is to determine the values of real water migration coefficients characterizing the mobility of chemical elements in the weathering process.

Before proceeding to the assessment of mobility of chemical elements, it is necessary to make some refinements concerning the compositions of weathered rocks and dissolved substances in the river and underground discharges. Based on the results of generalizing works on the chemical structure of the Earth's crust and on the content of dissolved forms of chemical elements in sur-

face and groundwaters of the intense water exchange zone, these refinements make it possible not only to introduce substantial corrections into the used numerical material but also to analyze the mobility of chemical elements in the global aspect, having reduced to a minimum the influence of local and regional geochemical characteristics of different territories.

Ronov and Yaroshevskii (1976) have generalized a vast factual material regarding the distribution and chemical composition of rocks in major tectonic zones of the Earth's crust. Within the boundaries of continents, these authors identified post-Riphean geosynclines, platforms, and shields with the pre-Riphean folded basement, for which the thicknesses of sedimentary, "granite" and "basalt" layers, as well as the relative distribution and average chemical composition of main rock types were calculated.

Since hypergene transformations occur within a thin surface layer with intense water exchange, only different areas of major structural elements of the Earth's crust should be taken into account in calculating the average chemical composition of rocks in the hypergenesis zone, having assumed that geosynclines and platforms are represented by sedimentary rocks, whereas shields are represented by rocks of the "granite" layer. Evaporite deposits represented by gypsum and salts (2.8% on platforms and 0.3% in geosynclines) play a noticeable role in the sedimentary cover of platforms and to a lesser extent in the cover of geosynclines. The possibility for prolonged preservation of these easily soluble minerals in the Earth's crust is connected with their location in the retarded water exchange zones characterized by slow weathering processes. Therefore, the elimination of evaporite deposits in calculating the average chemical composition of the hypergenesis zone is at first glance quite justified. However, the absence of evaporites in the intense water exchange zone is the result of natural geochemical pro-

**Table 1.** Chemical composition of rocks from major structural elements of the Earth's crust and the entire hypergenesis zone

| Component                      | Plates (37%) |       | Geosynclines (40%) |        | Shields (23%) | Hypergenesis zone |        |
|--------------------------------|--------------|-------|--------------------|--------|---------------|-------------------|--------|
|                                | a            | b     | a                  | b      |               | a                 | b      |
| SiO <sub>2</sub>               | 44.82        | 46.09 | 48.83              | 48.97  | 63.08         | 50.62             | 51.15  |
| TiO <sub>2</sub>               | 0.63         | 0.65  | 0.70               | 0.70   | 0.54          | 0.64              | 0.65   |
| Al <sub>2</sub> O <sub>3</sub> | 9.78         | 10.06 | 12.86              | 12.90  | 15.38         | 12.30             | 12.42  |
| Fe <sub>2</sub> O <sub>3</sub> | 2.54         | 2.61  | 2.51               | 2.52   | 2.24          | 2.46              | 2.49   |
| FeO                            | 2.04         | 2.10  | 3.06               | 3.07   | 3.60          | 2.81              | 2.83   |
| MnO                            | 0.070        | 0.072 | 0.109              | 0.109  | 0.095         | 0.091             | 0.092  |
| MgO                            | 3.82         | 3.91  | 3.11               | 3.12   | 2.96          | 3.34              | 3.38   |
| CaO                            | 14.11        | 13.98 | 12.70              | 12.68  | 3.79          | 11.97             | 11.12  |
| Na <sub>2</sub> O              | 1.28         | 0.68  | 1.65               | 1.59   | 2.71          | 1.76              | 1.51   |
| K <sub>2</sub> O               | 2.22         | 2.27  | 1.92               | 1.93   | 2.89          | 2.25              | 2.28   |
| P <sub>2</sub> O <sub>5</sub>  | 0.111        | 0.114 | 0.156              | 0.156  | 0.160         | 0.140             | 0.141  |
| C <sub>org</sub>               | 0.59         | 0.59  | 0.47               | 0.47   | 0.05          | 0.42              | 0.42   |
| CO <sub>2</sub>                | 11.99        | 12.30 | 8.67               | 8.70   | 0.81          | 8.09              | 8.22   |
| SO <sub>3</sub>                | 1.68         | 1.03  | 0.181              | 0.11   | 0.10          | 0.72              | 0.45   |
| S <sub>pyr</sub>               | 0.28         | 0.28  | 0.147              | 0.15   | 0.064         | 0.18              | 0.18   |
| Cl                             | 0.826        | 0.10  | 0.120              | 0.042  | 0.021         | 0.36              | 0.059  |
| F                              | 0.054        | 0.055 | 0.041              | 0.041  | 0.052         | 0.048             | 0.049  |
| H <sub>2</sub> O               | 3.17         | 3.10  | 2.76               | 2.75   | 1.46          | 2.61              | 2.58   |
| Total                          | 100.01       | 99.99 | 99.99              | 100.01 | 100.00        | 100.01            | 100.02 |

Note: (a) With regard for evaporites; (b) without regard for evaporites. The relative distribution area is indicated in parentheses.

cesses, and it would be evidently correct to consider the calculations taking into account evaporites as a characteristic of the chemical composition of the initial parental substrate, whereas the calculations excluding evaporites as a characteristic of rocks corresponding to a certain statistically averaged stage of the hypergene transformation. The results of two variants of the average chemical composition of rocks in the hypergenesis zone (Table 1) show that any essential differences are observed only for chlorides and sulfates, for which the exclusion of evaporite deposits leads to the average content diminishing by a factor of 6.1 and 1.3, respectively. Hence, a substantial uncertainty in calculating the average value of the water migration coefficient occurs only for chlorides.

In assessing the transfer of dissolved substances from continents, the majority of authors restrict themselves to the consideration of data on the river discharge, ignoring the underground discharge to the ocean. The magnitude of the latter is about 2400 km<sup>3</sup> yr<sup>-1</sup> (Zektser *et al.*, 1984), which is equal to ~6% of the river water discharge. Despite a moderate value of the underground discharge, it can affect substantially the discharge of dissolved substances, especially in basins located within arid zones. Thus, for the Caspian and Aral seas, where the groundwater discharge is only 1%,

the underground ionic discharge is equal to 25–27% (Zektser *et al.*, 1984). Another way of the water discharge from continents, the glacial discharge, is apparently of no real significance, first, due to a low mineralization of ice and, second, due to the fact that salts contained in it are chiefly associated with the transboundary transfer of oceanic cyclic salts and the precipitation of terrigenous aerosol with water-soluble components.

The average composition of groundwater in the hypergenesis zone was calculated by Shvartsev (1978) as a result of statistical processing of more than 20000 chemical analyses. According to his estimates, the average mineralization of groundwater in the hypergenesis zone is 430 mg l<sup>-1</sup>, which is in fairly good agreement with the data of Zektser *et al.* (1984) on the average mineralization of the underground discharge equal to 540 mg l<sup>-1</sup>. The discrepancy (~25%) can be connected both with the differences in the methods used for the factual material processing and with the fact that the data are, at least partially, referred to different territories. Nevertheless, the uncertainties occurring in this case in evaluating the total discharge of dissolved substances must not exceed 2–3%, since the bulk of salts is carried out with the river discharge.

**Table 2.** Chemical composition and genetic structure of the continental discharge

| Component        | Concentration, mg l <sup>-1</sup> |       |                       | Chemical discharge, Mt yr <sup>-1</sup> |              |       | Sources of chemical discharge, Mt yr <sup>-1</sup> |                   |            |
|------------------|-----------------------------------|-------|-----------------------|-----------------------------------------|--------------|-------|----------------------------------------------------|-------------------|------------|
|                  | River discharge                   |       | Underground discharge | River                                   | Under-ground | Total | Cyclic salts                                       | Economic activity | Weathering |
|                  | a                                 | b     |                       |                                         |              |       |                                                    |                   |            |
| Na               | 5.15                              | 2.05  | 45.5                  | 300                                     | 109          | 409   | 112                                                | 116               | 181        |
| K                | 1.3                               | 0.1   | 4.6                   | 58                                      | 11           | 69    | 4                                                  | 5                 | 60         |
| Mg               | 3.35                              | 0.3   | 18.6                  | 152                                     | 45           | 197   | 14                                                 | 16                | 167        |
| Ca               | 13.4                              | 1.3   | 43.9                  | 613                                     | 105          | 718   | 4                                                  | 63                | 651        |
| Cl               | 5.75                              | 2.5   | 47.0                  | 344                                     | 113          | 457   | 202                                                | 138               | 117        |
| SO <sub>4</sub>  | 8.25                              | 3.25  | 75.1                  | 480                                     | 180          | 660   | 28                                                 | 187               | 445        |
| F                | 0.10                              | 0.0   | 0.45                  | 4.2                                     | 1.1          | 5.3   | 0.01                                               | 0.0               | 5.3        |
| HCO <sub>3</sub> | 52.0                              | 1.0   | 174                   | 2210                                    | 418          | 2628  | 1                                                  | 50                | 2577       |
| SiO <sub>2</sub> | 10.4                              | 0.0   | 17.4                  | 434                                     | 42           | 476   | 0.0                                                | 0.0               | 476        |
| Fe               | 0.040                             | 0.0   | 0.547                 | 1.67                                    | 1.31         | 2.98  | 0.0                                                | 0.0               | 2.98       |
| Al               | 0.050                             | 0.0   | 0.279                 | 2.09                                    | 0.67         | 2.76  | 0.0                                                | 0.0               | 2.76       |
| Mn               | 0.010                             | 0.0   | 0.049                 | 0.42                                    | 0.12         | 0.54  | 0.0                                                | 0.0               | 0.54       |
| P                | 0.040                             | 0.068 | 0.058                 | 4.50                                    | 0.14         | 4.64  | 0.0                                                | 2.92              | 1.72       |
| Ti               | 0.003                             | 0.0   | 0.011                 | 0.13                                    | 0.03         | 0.16  | 0.0                                                | 0.0               | 0.16       |

Note: River discharge composition: (a) natural background, (b) anthropogenic contribution. The HCO<sub>3</sub><sup>-</sup> loss (adjusted to CO<sub>3</sub><sup>2-</sup>) during weathering will amount to 1267 Mt yr<sup>-1</sup>. The river discharge is adopted from (Meybeck, 1979; Martin and Meybeck, 1979; Savenko and Zakharova, 1997). The underground discharge is adopted from (Shvartsev, 1978).

At present, the most complete generalization on the exportation of dissolved substances with the river discharge belongs to Meybeck (1979), who identified the natural and anthropogenic components (Table 2). According to his calculations, the supply from anthropogenic sources increases the average concentration of ions by 2–44% (Ca<sup>2+</sup> by 7.3%, Mg<sup>2+</sup> by 9.0%, Na<sup>+</sup> by 39.8%, K<sup>+</sup> by 7.7%, Cl<sup>-</sup> by 43.5%, SO<sub>4</sub><sup>2-</sup> by 39.4%, and HCO<sub>3</sub><sup>-</sup> by 1.9%). The reliability of this contribution of anthropogenic sources of dissolved salts can be verified on the basis of information regarding the amount of recovered Cl-bearing minerals, since they are highly soluble and completely enter into land waters after the implication. The recovery of sodium chloride has remained during several last decades approximately at the same level equal to 160 Mt yr<sup>-1</sup> (*Industrial Statistic* ..., 1987), which corresponds to 97 Mt yr<sup>-1</sup> of chlorides. With regard for the recovery of potassium salts, the amount of anthropogenic chlorides should be increased by 20 Mt yr<sup>-1</sup>, and the total anthropogenic discharge of Cl will be equal to 117 Mt yr<sup>-1</sup>. According to Meybeck, the concentration of anthropogenic chlorides in the river discharge is 2.5 mg l<sup>-1</sup>. If the volume of water surface discharge is equal to 41 700 km<sup>3</sup> yr<sup>-1</sup> (*Mirovoi* ..., 1974), the discharge of anthropogenic chlorides will amount to 104 Mt yr<sup>-1</sup>, which is only 11% less than the evaluation based on the information regarding the

recovery of Cl-bearing minerals. Evidently, a part of the recovered chlorides enters into the underground discharge composition. Therefore, the real discrepancy between the above-mentioned evaluations is still smaller. This allows us to believe that the data of Meybeck on the chemical composition of river discharge and the contribution of anthropogenic sources sufficiently closely represent the facts.

The assessment of the role of cyclic salts in the chemical composition of the continental discharge is connected with the solution of two basic questions: (a) determining the total amount of marine salts transferred through the atmosphere onto continents and (b) clarifying the degree of fractionation of the salt composition in seawater during the formation of oceanic aerosol.

The first question was most comprehensively considered in the work of Petrenchuk (1979) who, on the basis of detailed analysis of data on the composition of cloudy water and atmospheric precipitation, gave the most substantiated assessment of the supply of cyclic salts from the ocean to the land equal to 367 Mt yr<sup>-1</sup>. The phenomena of fractionation have been poorly studied. Experiments carried out both directly with seawater and strong electrolyte solutions indicated that the formation of finest drop entrainment (spray) during the destruction of air bubbles at the water surface is accompanied by changes in the concentration ratios of dissolved substances (Khentov, 1979; Savenko, 1990). The general physicochemical theory of this extremely



**Table 3.** Water migration coefficients of chemical elements in the hypergenesis zone

| Element | Content in the mineral residue of weathering-related continental discharge, % | Content in hypergenesis zone rocks, %<br>(on the anhydrous basis) |       | Water migration coefficient |       |
|---------|-------------------------------------------------------------------------------|-------------------------------------------------------------------|-------|-----------------------------|-------|
|         |                                                                               | a                                                                 | b     | a                           | b     |
| Na      | 5.36                                                                          | 1.34                                                              | 1.15  | 4.0                         | 4.7   |
| K       | 1.78                                                                          | 1.92                                                              | 1.94  | 0.93                        | 0.92  |
| Mg      | 4.94                                                                          | 2.07                                                              | 2.09  | 2.4                         | 2.4   |
| Ca      | 19.27                                                                         | 8.20                                                              | 8.16  | 2.4                         | 2.4   |
| Cl      | 3.46                                                                          | 0.36                                                              | 0.059 | 9.6                         | 59    |
| S       | 4.40                                                                          | 0.48                                                              | 0.37  | 9.2                         | 12    |
| C       | 7.51                                                                          | 2.27                                                              | 2.30  | 3.3                         | 3.3   |
| F       | 0.16                                                                          | 0.049                                                             | 0.050 | 3.3                         | 3.2   |
| Si      | 6.59                                                                          | 24.29                                                             | 24.55 | 0.27                        | 0.27  |
| Ti      | 0.005                                                                         | 0.39                                                              | 0.40  | 0.013                       | 0.013 |
| Al      | 0.082                                                                         | 6.68                                                              | 6.75  | 0.012                       | 0.012 |
| Fe      | 0.088                                                                         | 4.00                                                              | 4.05  | 0.022                       | 0.022 |
| Mn      | 0.016                                                                         | 0.072                                                             | 0.073 | 0.22                        | 0.22  |
| P       | 0.051                                                                         | 0.063                                                             | 0.063 | 0.81                        | 0.81  |

Note: (a) With regard for evaporates; (b) without regard for evaporites.

interesting natural process has not been elaborated yet; however, there are serious reasons to believe that the phenomena of fractionation play a substantially smaller role for basic salt components of seawater than for microelements. The oceanic aerosol contains, on average, 15% of terrigenous material represented primarily by eolian products of the soil cover in arid continental regions containing water-soluble salts and cations in absorbed complexes (Savenko, 1994). As tentative calculations show, the amount of these terrigenous contaminants is quite sufficient for the explanation of minor differences in the compositions of dissolved salts in the oceanic aerosol and seawater (Savenko, 1990). In addition, a part of excess sulfates is associated with the oxidation of gaseous  $\text{SO}_2$  and volatile S-bearing organic compounds permanently present in the oceanic atmosphere. The strong enrichment of the products of drop entrainment (spray) in microelements attaining a factor of  $10^2$ – $10^4$  with respect to seawater is probably caused by the flotation transfer of fine biogenic suspension and dissolved organic matter, in which microelements are concentrated (Savenko, 1990). In seawater, only a small fraction of basic components is in the form of suspensions and in the form of organic matter compounds; therefore, their fractionation is extremely insignificant.

Hence, in calculating the fraction of cyclic salts in the continental discharge, it can be assumed as a justified approximation that basic salt components are carried out of the ocean without any noticeable fractionation and are supplied to the land in ratios similar to those in seawater.

The estimates of the river, underground, and total chemical discharge are presented in Table 2, where the genetic sources of dissolved substances (cyclic salts, economic activity, and weathering processes) are also distinguished. In this case, it was supposed that the relative contribution of anthropogenic sources is the same in the river and underground discharges, and the supply of salts at weathering was calculated by the difference between the total chemical discharge and the sum of cyclic salts and anthropogenic supply. It can be seen from Table 2 that the chemistry of continental discharge is primarily regulated by weathering processes. However, economic activity accounts for 30–40% of the total discharge of sulfates and phosphorus. For Na and Cl, apart from anthropogenic sources, the atmospheric transfer of sea salts is essential, and, as a consequence, the contribution of weathering diminishes to 39 and 26%, respectively.

The mobility of chemical elements in the hypergenesis zone can be characterized quantitatively by the water migration coefficients (Perel'man, 1989):

$$K_i = C_{i(w)}/C_{i(r)}, \quad (1)$$

where  $K_i$  is the water migration coefficient of the element  $i$ ;  $C_{i(w)}$  and  $C_{i(r)}$  are concentrations of the element  $i$  in rocks and dry mineral residue of waters draining these rocks, respectively. The estimates presented in Table 3 indicate that the incorporation of evaporite deposits into the hypergenesis zone affects substantially only the water migration coefficient of Cl, which in this case diminishes from 59 (the weathering crust without evaporites) to 9.6. For Na and sulfates the

decrease of water migration coefficients is only 15 and 23%, remaining within the accuracy limits of the initial data. The water migration coefficients of all other elements have the same values in both models.

The model of water migration coefficients, from which evaporate deposits were excluded, seems to correspond better to real conditions, since all gypsiferous and saliferous deposits in the intense water exchange zone can be completely dissolved during a period of about  $10^5$  yr. This circumstance suggests that the observed chemical composition of continental discharge forms at present without any substantial participation of evaporites. Of course, a certain portion of dissolved salts is supplied from deeper strata of the sedimentary cover, where evaporite deposits and associated highly concentrated brines are present; however, this source of salts cannot be of any essential consequence due to a low intensity of the vertical water exchange in such structures.

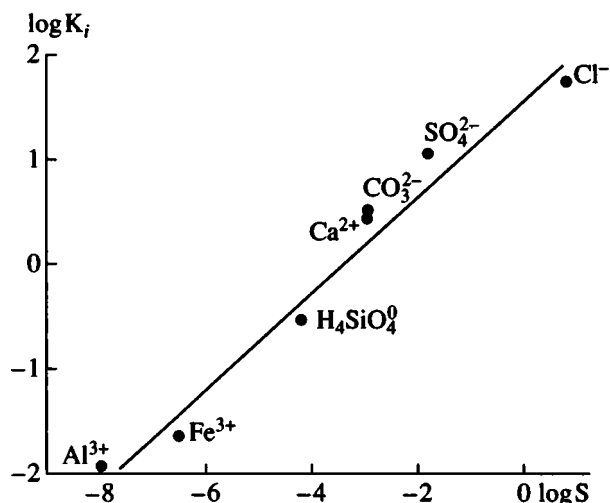
Arranging chemical elements in decreasing order of the water migration coefficients (Table 3), one may note that generally this series corresponds to the decreasing order of solubility of major hypogene minerals. We tried to characterize quantitatively the specified relationship on the basis of the following data. The water migration coefficients of Cl and S were compared to the solubility of halite and gypsum, the water migration coefficient of carbonate C was compared to the solubility of calcite at the atmospheric pressure of  $\text{CO}_2$ , and the water migration coefficients of Fe and Al were compared to the solubility of corresponding hydroxides (Lur'e, 1989; Naumov *et al.*, 1971; Mel'nik, 1972). The  $\text{H}_4\text{SiO}_4$  concentration in the solution at equilibrium with the paragenetic gibbsite-kaolinite association (Shvartsev, 1978; Drever, 1985) was used for Si. As seen from the figure, the dependence

$$\log K_i = 1.634 + 0.462 \log S \quad (2)$$

is actually observed between the water migration coefficient and the solubility of minerals ( $S$ ,  $\text{mol l}^{-1}$ ).

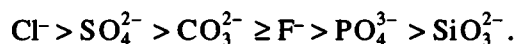
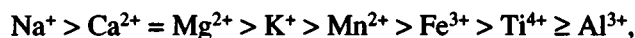
It should be stressed that equation (2) does not reflect a cause-and-effect relationship; the mobility of chemical elements in the hypergenesis zone depends on many simultaneously acting physical, chemical, and biological factors, whereas the solubility of major hypogene minerals serves only as a characteristic of the water-absorbing capacity of elements, i.e., the property expressed to some extent in all hypogene processes indiscriminately and reflecting the capacity of elements to pass into the dissolved state.

Hence, the account for marine cyclic salts and anthropogenic sources in dissolved substances of continental discharge makes it possible to assess the real mobility of chemical elements in the hypergenesis zone. According to their water migration coefficients, cations and anions can be arranged in the following decreasing order of the hydrophilicity (water-absorbing



Water migration coefficient ( $K_i$ ) vs. solubility value ( $S$ ,  $\text{mol l}^{-1}$ ) for major hypogene minerals.

capacity) of elements:



In this case, the mobility of chemical elements directly depends on the solubility of their main hypogene minerals in the region.

## ACKNOWLEDGMENTS

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## Nickel Ores in the Urals

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**Abstract**—Based on the analysis of long-term openpit observations of nickel oxide–silicate ores and literature data, characteristic features of the nickel mineralization and raw mineral base for the nickel industry in the Urals are given. The present-day critical situation in this field is outlined and means of the prospecting for high-grade nickel ore deposits in the Urals are proposed. The development of such deposits should be feasible under conditions of the modern market economy.

The Ural region is second to the Noril'sk–Talnakh mineral resource base for the nickel industry in Russia. Mining plants in Rezh, Ufalei, Orsk, and Svetlyi Settlement are specialized in processing hypogene cobalt–nickel oxide–silicate ores that are typical for the Ural region (Fig. 1).

In the Urals, nickel ores were discovered as early as the 1850s (Naboichenko, 1996). The issue of the construction of a nickel plant in the Urals was discussed after the World War I. However, this plan was adversely affected by the October Revolution and subsequent devastations in Russia. The construction of the first nickel plant in Verkhniy Ufalei in 1933 marked the beginning of the nickel and associated cobalt industry in our country.

The first geoeconomic review, which was published at the beginning of the 1930s and devoted to the state of nickel mineral base in the Urals, disclosed the fact that the first technological project of nickel production was based on the supply of oxide–silicate ores with an average Ni content of no less than 4.5% (Glazkovskii, 1932). The technological scheme designed in 1933 for the Ufalei nickel plant envisaged the smelting of ores with a Ni content of 2.5–2.75%. As high-grade ores of the Ufalei district became exhausted, technical requirements for the ore that was supplied to the Ufaleinikel Plant or other younger nickel plants were appreciably reduced.

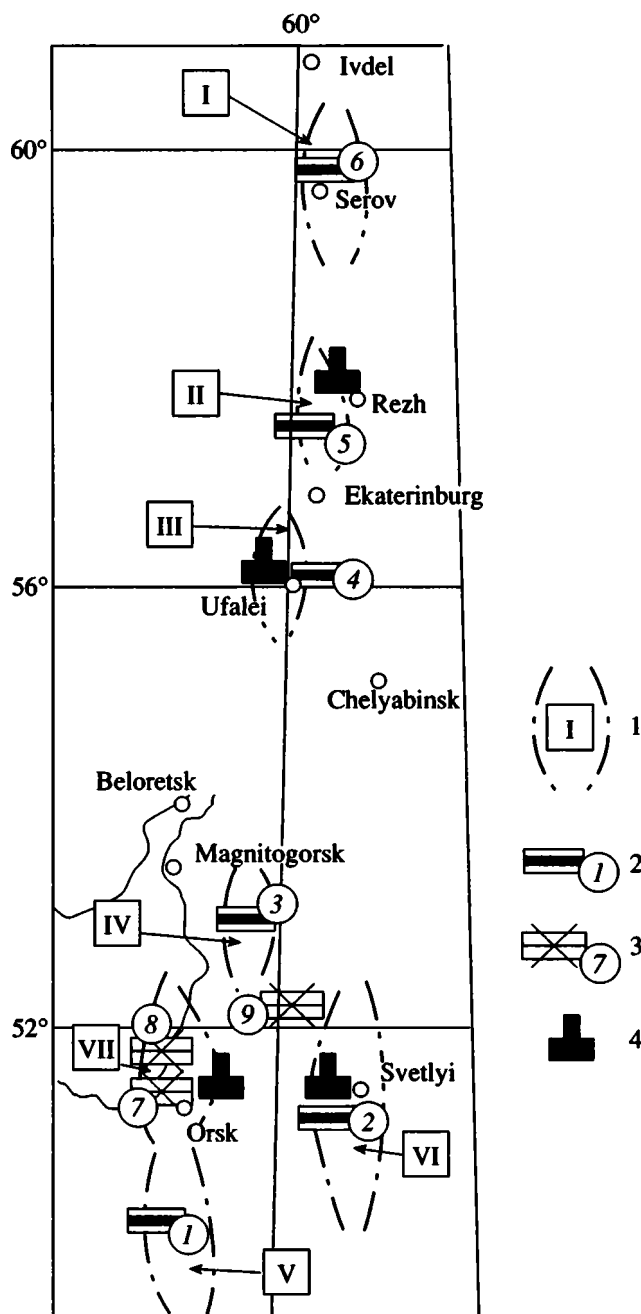
Under the socialistic planned system of economy, nickel was qualified as a strategic metal. The feasibility of its production in the Urals was never discussed, since the strategic metal industry always received unlimited subsidies (Stukalov and Muftanov, 1996). The metal equivalent reserves of hypogene nickel ores were estimated at several hundreds of thousands of tons, which were sufficient enough for the continuous functioning of nickel plants for several decades.

In 1985, we were the first to carry out a quantitative appraisal of potential nickel resources in the Urals. The total sum of nickel resources ( $1750 \times 10^3$  t) is distributed among the following districts ( $10^3$  t): (I) Serov dis-

trict 350; (II) Rezh district 150; (III) Ufalei district 100; (IV) Sakharin district 400; (V) Kempirsai district 300; and (VI) western Turgai district, including the Buruktal area 450 (Karta..., 1985). We had concluded in the report that potential nickel resources in the region are mainly represented by low-grade ores (Ni <1%) that are located at depths of more than 200 m and, therefore, are not suitable for openpit mining. The quality of explored reserves at deposits under exploitation, however, was more or less satisfactory (Table 1).

The situation in the nickel industry of the Ural region suffered a severe change after the breakdown of the Soviet Union and the introduction of market economy system in Russia. Owing to several reasons (low grade of ores, exhaustion of reserves at deposits, increasing distances of haul, and others), practically all probable resources and a significant portion of proven reserves turned out to be below the competitive level, relative to foreign counterparts (Table 2). Consequently, the nickel industry became unprofitable in the Urals (Naboichenko *et al.*, 1996). Currently, nickel plants are supplied with low-grade ores from operating mines. The Ni content in present-day ores is as follows (%): Serov deposit (Elov openpit) 0.82; Buruktal deposit 0.64; and Sakharin deposit 0.91 (Proshin and Gorelov, 1997). Ores from the Kempirsai deposit, which is now located in the Kazakhstan territory, are supplied at the world price level, which is not profitable for us. The Republic of Cuba suspended the export of concentrates that served as raw mineral base for nickel plants at the Svetlyi Settlement and other places during several years.

The Geological Survey of Russia is now facing a complicated problem concerning the fundamental revision of present concepts of nickel ore reserves and resources in the Urals, along with the development of a comprehensive program of prognosis and prospecting for high-grade ore deposits in economically favorable regions, i.e., the discovery of deposits that can reanimate nickel industry in the Urals.



**Fig. 1.** Schematic location of ore districts in the Uralian Ni-bearing province. (I) Ore districts: (I) Serov; (II) Rezh; (III) Ufalei; (IV) Sakharin; (V) Kempirsai; (VI) Buruktal; (VII) Khalilov; (2) operating deposits: (1) Kempirsai; (2) Buruktal; (3) Sakharin; (4) Ufalei group; (5) Lipov; (6) Serov group; (3) exhausted deposits: (7) Akkermanov; (8) Aiderbak; (9) Aidylrin; (4) nickel plants.

Most researchers believe that nickel ore deposits in the Urals belong to the surficial hypergenesis type; i.e., they are related to weathering crust and eluvium redeposition in karst depressions (*Prognoznaya ...*, 1998). Nickel is allegedly concentrated in eluvium as a result of the accumulation of this metal but removal of Si and

Mg during the weathering of rocks, along with a partial migration of Ni along the weathering crust profile. The exclusive assignment of commercial-grade deposits to dunite-harzburgite massifs is explained by high Ni concentrations in ultrabasic rocks.

Based on our 30-year-long experience of the study of various deposits in the world, in all cases of the development of weathering crust on ultrabasic rocks, which were not definitely (or probably) transformed by deep thermal waters, the average Ni content in eluvium generally amounts to 1.1–1.3%. The content rises to 1.4–1.5% only in the Earth's tropical belt with lateritic sedimentary covers. Figure 1 shows that deposits, where orebodies with the Ni content of 2–3% are developed, usually incorporate Ni-bearing veins related to thermal hypergenesis (e.g., veins in New Caledonia, Ufalei, and others) or elevated concentrations of nickel sulfides in the substrate (Lipov, Aiderbak, and other deposits).

In the Urals, relative to the Cenozoic tropical zone of the Earth, the lateritic process was only weakly developed in the Mesozoic. Therefore, we suppose that it is hardly possible to discover purely crust-related, almost horizontal orebodies with elevated Ni concentrations (at least >1.2–1.4%) in this region.

Giant nickel resources amounting to hundreds of thousands or even millions of tons, which were accepted by the Ministry of Geology of the Soviet Union and are now adopted by the Ministry of Natural Resources of Russia, are characterized by Ni concentrations up to 0.9–1.1%. Such low-grade ores cannot be feasible under market economy conditions.

Therefore, we propose a different method for solving the problem of raw mineral base for nickel industry in the Urals. Our proposals are based on the following observations. The nickel ore formation in the Urals was a polychronous and polyfacies process. In addition to low-grade nickel ores associated with Cretaceous–Paleogene, almost horizontal (areal), weathering crusts in ultrabasic massifs, high-grade oxide–silicate ores produced in other settings and age intervals are also known in this region. Deposits related to thermal hypergenesis represent the most essential example (Mikhailov, 1997). Of particular interest is the problem of prospecting for endogenic Paleozoic nickel sulfide ores in the Urals, since such ores can stimulate the development of high-grade oxide–silicate ores in the weathering crust.

#### FEATURES OF NICKEL MINERALIZATION IN THE URALS

The Ural region incorporates a genetic series of numerous nickel ore deposits and occurrences, which accompany the evolution of ultrabasic massifs from their origination in the upper mantle to complete destruction in autonomous topography depressions. The latter were formed in the Ni-bearing eluvium dur-

**Table 1.** Cut-off grade and minimal commercial contents of metals for major deposits of nickel oxide-silicate ores, % (Matveev, 1969)

| Ore district | Deposit         | Content |             | Cut-off grade | Minimal commercial content | Major components |
|--------------|-----------------|---------|-------------|---------------|----------------------------|------------------|
|              |                 | Ni      | Co          |               |                            |                  |
| Kempirsai    | Kempirsai group | 1.110   | 0.036–0.055 | 0.7–0.9       | 1.1                        | Ni               |
|              |                 | 1.28    |             |               |                            |                  |
| Ufalei       | Ufalei group    | 1.08    | 0.026       | 0.7           | 1.1                        | Ni               |
|              |                 | 1.26    | 0.024       |               |                            |                  |
| Rezh         | Lipov           | 1.54    | 0.057       | 0.7           | 1.1                        | Co + Ni          |
| Khalilov     | Aiderbak        | 1.06    | 0.073       | 0.7           | 1.1                        | Co + Ni          |

ing the Mesozoic–Cenozoic stagnation. All members of the series have an affinity to dunite–harzburgite massifs, in which the magnesian group ( $\text{MgO} : \text{FeO} > 9$ ) is characterized by primarily high Ni contents (up to 0.33%) and serves as a favorable substrate for diverse hypogene deposits.

The genetic relation of ultrabasic rocks and gabbroids of the dunite–harzburgite association with compositionally different dikes and the frequent occurrence of nickel sulfides in them suggests that these rocks can incorporate commercial deposits of endogenous nickel sulfide ores.

The Paleozoic history of the Urals foldbelt was repeatedly interrupted by injections of ultrabasic magma and intrusion of ultrabasic bodies along deep fracture zones. The anionic portion of pneumatolytic-hydrothermal fluids associated with the Paleozoic magmatic activity contained abundant sulfur that was realized as anomalous concentrations (ore occurrences and even deposits) of chalcophile metals (Fe, Cu, Pb, Zn, Ni, and others) along fluid percolation zones. At present, Paleozoic fractures with the sulfide mineralization are distinctly outlined by extended melange zones and ultrabasic belts.

During the Early Mesozoic tectonomagmatic activation of the Urals, the magmatic (endogenic) activity and rejuvenation of deep fractures were characterized by specific features. The thermal regime was less intense, and the hydrothermal activity was only manifested in local sectors (thermal windows) that commonly represented almost vertical, tens to hundreds of meters in diameter, conduits located in ancient melange zones. The composition of hydrothermal solutions percolating along them was governed by the hydrolysis of melange rocks. Thermal (carbonate gleyey) waters infiltrating in the carbonate–serpentinite melange were evidently very favorable for the leaching, transfer, and precipitation of Ni. In this case, the hypogene zone was supplied with practically S-free, siliceous–carbonate waters, in which the cationic portion contained bivalent Fe, Mn, Ni, and Mg. Some elements (Si, Ni, and Mg) precipitated from solutions at hypogene barriers of pressure and temperature drops, resulting in the forma-

tion of various hydrosilicates (garnierite, kerolite, sulgunite, and others), chalcedony, and quartz. Other elements (e.g., Fe and Mn) remained in the bivalent state and migrated toward the subsurface oxidation zone. At the hypogene oxidative barrier, they precipitated in the form of iron and manganese hydroxides (goethite, hydrogoethite, bog manganese, pyrolusite, and others) and made up siliceous ocher accumulations together with silica.

Thus, the hypogene section is composed of two zones. The lower reductive (Fe-free) zone includes garnierite (kerolite) and quartz. The Ni content in this zone is high (3–5% or more). The upper (ocherous) zone has a lower Ni content (0.5–0.7%). The boundary between these zones is generally intricate. Ramified Ni-bearing reductive waters occasionally injected into the reductive zone and even reached the day surface (Mikhailov, 1997). The Fe-free quartz–garnierite ores related to thermal hypogenesis represent the intermediate member between sulfide (endogenic) and oxide–silicate (eluvial and infiltrational-sedimentary) nickel ores.

The Uralian platformal history, which postdated the Early Mesozoic tectonomagmatic activation, was characterized by an extensive development of physico-chemical environments that were favorable for the formation of eluvium. Weathering crusts developed on ultrabasic massifs during this time incorporate the large

**Table 2.** Main indicators of the raw mineral base of oxide-silicate ores in the world

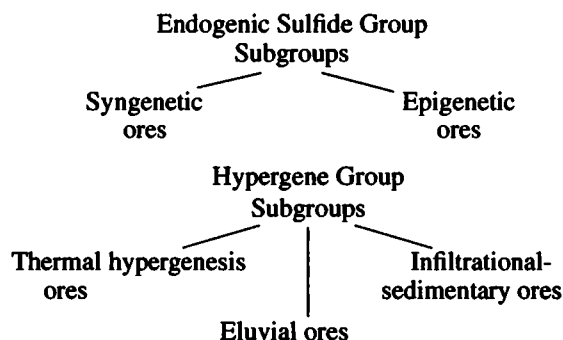
| Country              | Ni reserves, Mt | Ni production, kt | Ni content in ore, % |
|----------------------|-----------------|-------------------|----------------------|
| Cuba                 | 18.000          | 40.0              | 1.10–1.16            |
| New Caledonia        | 11.700          | 121.0             | 2.10                 |
| Indonesia            | 2.960           | 88.2              | 1.60                 |
| Philippines          | 0.370           | 3.5               | 2.10                 |
| Columbia             | 0.450           | 24.0              | 2.60                 |
| Russia (Ural region) | –               | 8.0–10.0*         | 0.71                 |

\* The estimate is adopted from (Proshin and Gorelov, 1997).

est hypogene deposits with low-grade ores (Ni 0.7–1.1%).

Meanwhile, nickel was accumulated in a reductive, sometimes organic-rich environment of bogs and stagnant basins within Ni-bearing weathering crusts or karst depressions. Therefore, the metal was adsorbed by the mineral substrate, resulting in the formation of a specific group of sorptional deposits that are commonly referred to as the infiltrational-sedimentary depression type (according to Grigor'eva, 1967).

Thus, the genetic series of nickel mineralization in the Urals can be divided into the following groups and subgroups:



The practical implication of above-listed groups is diverse. Currently, only remnants of eluvial ore deposits and small orebodies related to thermal hypergenesis are mined. The prospecting for endogenic sulfide ores in the Urals during the 1930s–1960s was unsuccessful, although chances for the discovery of commercial endogenic deposits are quite realistic. Small bodies of infiltrational-sedimentary sulfide ores can be found in erosion-karst valleys and depressions within the Ni-bearing eluvium, or along tectonic contacts between Ni-bearing plutons and carbonate rocks.

## ENDOGENIC SULFIDE ORES

Basic and ultrabasic rocks, which are of interest in the prospecting for nickel sulfide mineralization in the Urals, are clustered as submeridional belts confined to deep regional fractures and thrusts. The largest fractures are located in eastern zones of the Urals, i.e., in marginal sectors of the Magnitogorsk and Tagil troughs. Sulfide mineralizations of the Ni, Co, rare metal, and other types are encountered in almost all large massifs; however, presently none of them is of practical interest.

The genetic concept accepted by most researchers suggests that nickel sulfide mineralization cannot be developed in the Ural-type structure. The intense dislocation of plutons, coupled with their repeated displacements and transformations in a restless Paleozoic environment in the Urals, were obviously unfavorable for the formation of large liquation-type orebodies that are known in the Noril'sk–Talnakh region. Therefore, one can hardly expect commercial syngenetic deposits of

nickel sulfide ores in the Urals. However, epigenetic (both veined and disseminated) ores can be discovered in several ore districts.

This assumption is supported by works devoted to the study of copper–nickel mineralization in gabbroid and ultrabasic massifs within geosynclinal rifts of the Urals, Zaisan, and other fold systems (Kolotilov and Petrov, 1988). Special attention is given to the Kempir-sai and other magmatic complexes of the alpine-type gabbro–peridotite (harzburgite–dunite) association and the Khabarnin Complex of the dunite–pyroxenite–gabbro association (Fig. 1). Particular emphasis is placed on the mantle source of ore material, its concentration in the major and intermediate magmatic centers, and the subsequent displacement and injection of the ore-forming melt (Kolotilov and Petrov, 1988, p. 52). Favorable prospecting guides include (1) the association of ultrabasic–gabbro massifs with high-Mg subalkaline rocks and (2) the presence of sulfide mineral assemblage (pentlandite, chalcopyrite, troilite, and other magmatic and hydrothermal minerals).

Based on existing concepts of the deep structure (Berlyand, 1993) and petrography of rock massifs in the Ural region, we assume that the Khalilov, Rezh, and Ufalei ore districts can be favorable for the discovery of sulfide ore deposits (Fig. 1).

The **Khalilov ore district**, situated at the western flank of the Orsk Depression, includes the Khalilov, Khabarnin, Baiguskarov, and Katralin massifs (Nikitin *et al.*, 1970; Buchkovskii, 1960; and others). Of particular interest is the following fact. In 1927, geologists had found a unique schlieren (probably lense) of massive sulfide ore in the Khalilov Massif. The schlieren, 0.3–0.6 m thick and approximately 4 m long along the dip, yielded 13 t of sulfide ore with a Ni content of 20–24% (Shadlun, 1929; Ul'yanov, 1934; and others). Different-scale nickel sulfide occurrences were encountered in all rock massifs of the district (Ul'yanov, 1934; Buchkovskii, 1960; Dmitriev, 1963; Sheshukova, 1969; and others).

The **Rezh and Ufalei ore districts** in the northern Urals are confined to the Uralian Major Thrust Zone (MTZ). They also incorporate numerous nickel sulfide ore occurrences (Fig. 1). Recently, Kudryashov revealed a genetic relationship between sulfide ores and the high-grade quartz–garnierite mineralization within the Lipov deposit, the Rezh ore district (Kudryashov and Maleev, 1996).

We suppose that massifs of the Serov ore district, which are also confined to the Uralian MTZ, as well as the Sakharin and Aidyrilin massifs in the eastern Magnitogorsk Megasyntlinorium, deserve special attention, since they include nickel sulfide occurrences with a Ni content up to 0.4%.

Not a single ultrabasic massif in the Urals was comprehensively examined for the nickel sulfide mineralization. Boreholes drilled on these massifs up to the 1960s (i.e., prior to the discovery of the Talnakh deposit



in the Noril'sk district) only reached a depth of 100–200 m. After the penetration of very high-grade, compound nickel sulfide ores by pioneer boreholes in the Talnakh area, prospecting for nickel sulfide ores in the Urals was practically halted.

## HYPERGENE ORES

### *Thermal hypergenesis ores*

Lodes of the highest grade nickel oxide–silicate ores in the world were first discovered on New Caledonia Island as early as the 19th century. Their mining was started in 1875 (Glasse, 1903–1904). During the 1910–1920 period, ore fields of this island yielded  $900 \times 10^3$  t of ores with a Ni content of 6.5% (*Le Gisements...*, 1978). Orebodies, now completely mined, represented veins or linear stockworks, 10 to 20 m thick and more than 150 long along the dip. Ores consisted of serpentinite breccia with a ferruginous matrix. Serpentinite, partially altered by kerolite, was associated with quartz, chalcedony, prasopall, talc, serpentine, and carbonates. The ore composition was as follows (%):  $\text{SiO}_2$  42–50,  $\text{Fe}_2\text{O}_3$  15–20,  $\text{MgO}$  20–32, and  $\text{NiO}$  5–10. Following the first explorers, many investigators refer these veined, so-called tectonic nickel ores to the hydrothermal type.

The top of nickel orebody is commonly covered by eluvium, which also represents a Ni-bearing (although low-grade) sediment. The export-oriented mining in New Caledonia produced compound ores with a Ni content of 2 to 3%. Miners were not interested in genetic aspects. A somewhat similar situation originated later in Russia. As early as 1930s, two apparently irreconcilable concepts of the genesis of cobalt–nickel ore deposits, which were discovered by that time in the Urals, dominated the Russian geological community.

The majority headed by prominent scientists (I.I. Ginzburg, I.I. Savel'ev, N.P. Kheraskov, F.F. Sysoev, and I.Z. Korin) and followed by younger proponents (K.K. Nikitin, Yu.Yu. Bugel'skii, I.I. Edel'shtein, A.M. Kudryashov, K.G. Borodina, I.V. Vitovskaya, and others) believed that all hypergene nickel oxide–silicate ores, which are known in the world, are characterized by the exogenic (eluvial) genesis. The minority (V.V. Nikitin, A.N. Aleshkov, D.G. Ul'yanov, as well as our contemporaries V.N. Razumova, A.S. Vershinin, and the author of this work) did not reject the eluvial genesis of orebodies at most deposits under operation but assumed that the highest grade, cobalt–nickel silicate (siliceous–ferruginous quartz–garnierite) ores were formed with an active involvement of thermal waters.

As long ago as 1932, Ul'yanov reported the hydrothermal precipitation of nickel sulfide ores in the Khalilov deposit and emphasized that the final hydrothermal stage is characterized by the precipitation of high-temperature quartz and opal. Silica stringers, which are formed during this process, locally include a nickel

mineral (probably garnierite) that was crystallized after nickel sulfide as a result of the disappearance of sulfur from solutions, since the entire sulfur volume was connected with Ni at the first stage (*The Khalilov ...*, 1932, p. 46).

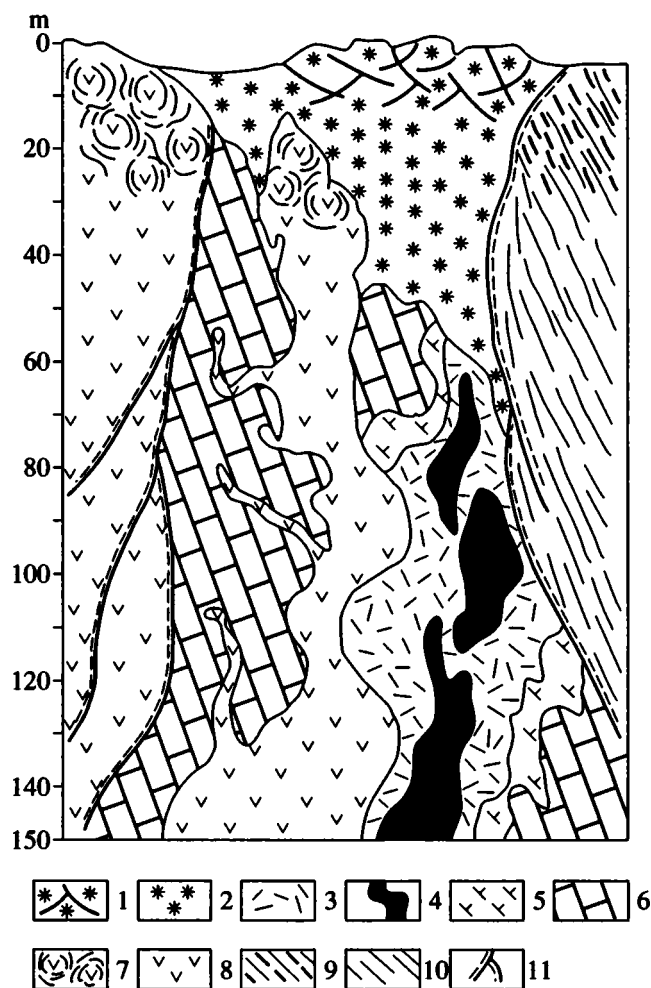
In the 1970s, Razumova (1977) carried out a comprehensive analysis of the role of hydrothermal waters in the formation of so-called fissure-zone (or linear) weathering crusts. She revised concepts of surficial (eluvial) origin and proposed the hydrothermal–vadose genesis of ancient weathering crusts. According to this hypothesis, ancient weathering crusts are linked to deep centers of the discharge of confined waters and represent upper marginal facies of hydrothermal systems, i.e., products of the metasomatic leaching, replacement, and cementation in sites where groundwaters mix up with endogenic emanations from deep, active, and steep fractures in the basement (Razumova, 1977, p. 8).

In the 1990s, we carried out investigations at deposits of the Ufalei ore district and checked earlier contradictory concepts of rock and ore formation in the hypergene zone (*Izuchenie...*, 1995). The obtained results made it possible to reconcile these concepts and propose an alternative model for the Ufalei-type nickel ore deposits associated with linear (karst- and fracture-zone) weathering crusts (Mikhailov, 1997).

According to this model, nickel orebodies originated in marginal sectors of the Magnitogorsk Megasyntinorium during the Early Mesozoic activation that produced intense fracture zones and central-type hydrothermal systems near ultrabasic massifs. The ore material was mainly accumulated in stock-shaped conduits of metalliferous hydrothermal solutions, i.e., in “thermal windows” confined to rejuvenation sectors of ancient fractures. Stocks hosting nickel ore deposits are generally registered on the day surface as rounded bodies of crushed material that is intensely hydrated down to a depth of several hundreds of meters. The stocks are embedded within unaltered or slightly altered rocks of basement that is locally devoid of weathering crust. The ore material is precipitated from ascending  $\text{CO}_2$ -rich hydrothermal solutions at hypergene barriers, such as *PT* drop, pH and Eh changes, colloidal-sorptional barrier, and others.

The Chusov orebody of the Cheremshan deposit (Ufalei district) is a typical example of orebodies related to thermal hypergenesis (Mikhailov, 1997). By the year 1997, the orebody was mined to a depth of 280 m. Borehole data indicate the presence of high-grade ores (Ni >4.5%) at 410 m. On some benches of the abandoned openpit, one can observe fragments of hydrothermal karst cavities, along which ore-bearing solutions ascended during the hydrothermal system functioning (Fig. 2).

Another example is provided by the Akkermanov deposit (Khalilov ore district) located in the eastern Khabarnin ultrabasic massif (Guberlin Mountains) on



**Fig. 2.** Schematic drawing of the northeastern wall of the Chusov openpit, Cheremshan deposit, Ufalei ore district (as of Aug. 1997). (1) Cavemous limonite; (2) ocher, locally silicified; (3) hydrothermal-karst (silty-clayey) rock (Ni 0.6–1.3%); (4) large nodules and concretions of quartz-garnierite ores (Ni 2.0–10% or more); (5) kerolitized marble; (6) marble; (7) slightly hydrated serpentinite with nucleus structure; (8) serpentinite; (9) black (hydrated) chlorite-sericite schist; (10) black (carbonaceous) chlorite-sericite schist; (11) detachment lines and slickensides in rocks with gouges.

the right bank of the Ural River (Fig. 1). The ore deposit is confined to a large tectonic dislocation represented by a 200- to 250-m-wide and approximately 2 km long tectonic breccia zone. The main fault, which is a subsidiary of the Uralian MTZ, steeply dips to east at an angle of 70°–80°. It has an asymmetric structure. The western wall is a tectonic breccia band of intensely altered, locally grinded and schistosed serpentinites with magnesite interlayers. To the west, the breccia are replaced by strongly crushed and kerolitized serpentinites. The eastern hanging wall is a retiform breccia band of low-altered, apoperidotite, angular serpentinite fragments cemented by dolomite stringers.

Outcrops of the ore zone are marked by a 30- to 50-m-high ridge. The ridge consists of friable ores and stands out against the background of low-altered, massive, native serpentinites. The friable ores could resist erosion owing to the presence of a quartz matrix.

The ore alteration is maximal near the thrust plane and attenuates in both lateral zones. Although the horizontal cross-section of orebodies has an irregular-isometric form, their meridional orientation is preserved. The middle sector of orebodies commonly consists of variegated, intensely folded, and hydrated serpentinites with large birbirite concretions crosscut by a network of fine calcite and garnierite stringers. Ore stringers are usually confined to slickensides (Ul'yanov *et al.*, 1937). Since the deposit has only been studied by boreholes to a depth of 100–150 m, we cannot confidently judge the attenuation level of ore generation.

Relative to counterparts from the Ufalei ore district, the Akkermanov deposit, which also comprises the Ufalei-type assemblage of rocks and ores, has several distinctive features. The drilled melange zone completely lacks carbonate rocks and hydrothermal karst cavities that could be infilled with structureless but medium-grade, nickel oxide-silicate ores.

Based on the exploration and mining data, ores of the Akkermanov deposit can be divided into the following two major types.

(1) Magnesian ore with a high Mg content ( $\text{MgO} > 20\%$ ) and low Fe content ( $\text{Fe}_2\text{O}_3$  10–20%). This type includes the high-grade calcite-garnierite ore in stockworks.

(2) Quartz-ferruginous ore with  $\text{MgO} < 10\%$  and  $\text{Fe}_2\text{O}_3$  equal to 30–70%. This ore is confined to central fissure zones. The ore is composed of dark brown, massive ochreous rock (with relics of pyroxene), light yellow to reddish brown, massive ochers (with remains of green bastite grains), and massive (sometimes schistosed) but generally structureless ochers. The structureless ocher includes large quartz concretions of usually ferruginated, massive, or skeletal formations (birbirites). Cracks and cavities in ores include the major rock crystal and amethyst, the occasional calcite, pyrolusite, and wads, and the rare garnierite stringers and patches with high Ni concentrations ( $> 2\text{--}3\%$ ).

The eluvial genesis of the Akkermanov deposit is not supported by the following specific features of ores revealed in the 1930s–1940s (Ul'yanov *et al.*, 1937): (1) the selective nature of alterations during the metamorphism of pyroxene and olivine; (2) the confinement of ore-forming processes to local tectonic zones and the complete absence of mineralization in host ultrabasic rocks and typical weathering products; (3) the occasional coexistence of totally disintegrated (hydrated) and almost unaltered grains of the same mineral within a single thin section; (4) the zonal distribution of quartz, pure carbonates, and magnesium carbonates (it depends on the tectonic setting of the deposit); (5) the development of secondary (hydrothermal) minerals,

**Table 3.** Mineral contents in commercial ore types, % (Grigor'eva, 1969)

| Minerals                                 | Ore types   |                | magnesian |
|------------------------------------------|-------------|----------------|-----------|
|                                          | ferruginous | ferromagnesian |           |
| Nontronites                              | 5           | 70             | 15        |
| Iron hydroxides                          | 70          | 10             | 5         |
| Silica minerals                          | 5-30        | 5              | 10        |
| Serpentines                              | 5-10        | 10             | 60        |
| Clay minerals (kaolinite and halloysite) | 5-10        | —              | —         |
| Manganese minerals                       | 3-5         | 3              | 1-2       |
| Nickel silicates                         | —           | —              | 3-4       |
| Orthochlorites                           | —           | 5-7            | —         |

such as chlorite, talc, and micas; (6) the specific mineralization sequence (the early quartzification is successively followed by ore mineralization and late carbonatization); and (7) the active character of quartz-replacing solutions.

The polychronous formation of commercial orebodies is distinctly manifested at the Akkermanov deposit. The evolution of this deposit can be divided into three stages.

(1) The Late Paleozoic (Middle to Late Carboniferous) stage was characterized by the origination of the Uralian MTZ, the intrusion of ultrabasic bodies, and the formation of serpentinite melange zones.

(2) The Early Mesozoic (primarily Late Triassic) stage was noted by the tectonomagmatic activation, the formation of thermal windows in the serpentinite melange, the injection of Ni-bearing hydrothermal (carbonate-gleyey) solutions into the hypergene zone, and the formation of orebodies related to thermal hypergenesis.

(3) The Late Mesozoic (primarily Aptian-Cenomanian) stage was characterized by the intense development of Ni-bearing weathering crusts on ultrabasic rocks in the middle and southern Urals, the origination of high-grade oxide-silicate orebodies in eluvium on the Ni-rich substrate (endogenic sulfide mineralization and outcrops of Ni-bearing products related to thermal hypergenesis).

Each stage is characterized by the development of a specific mineral group. For example, according to D.G. Ul'yanov, G.S. Gritsaenko, and G.A. Krutov, the first stage includes chrysotile, brucite, and aragonite; the second stage includes ferruginous quartz, garnierite, rock crystal, amethyst, and morion; and the third stage includes nontronite, revdinskite, kerolite, magnesite, asbolanes, and wads (Ul'yanov *et al.*, 1937).

**Eluvial ores.** Eluvial ores in the Urals represent the major commercial type. At present, they are mined at three operating openpits located in the Buruktal, Sakharin, and Kola (Serov group) ultrabasic massifs (Fig. 1). In the Buruktal and Sakharin massifs, the gen-

eralized profile of the Ni-bearing weathering crust comprises the following zones (from bottom to top): (1) leached serpentinites; (2) nontronitized (kerolitized) serpentinites; (3) nontronites; and (4) ochers (Ginzburg *et al.*, 1946; Nikitin *et al.*, 1970; Vershinin, 1996; and others). Some sectors are characterized by the presence of horizons or lenses of silicified, carbonatized, and intensely ferruginated serpentinites, magnesite interlayers, nickel hydrosilicates, opal stringers, quartz, and iron and manganese hydroxides. The ore mineralization can be registered in each zone or horizon. The position of orebodies in the weathering profile appreciably governs the mineral composition and technological features of ores. One can usually recognize three (ferruginous, ferromagnesian, and magnesian) commercial ore types (Table 3).

#### DEPOSITS OF THE BURUKTAL MASSIF

The Buruktal Massif, situated in the southeastern Orenburg district near the boundary with Kazakhstan, has the following parameters: total area 350 km<sup>2</sup>, length (from southwest to northeast) ~35 km; maximal width 12 km. Its Ni potential was comprehensively studied by K.K. Nikitin and I.I. Edel'shtein. Additionally, specific features of the massif and enclosed nickel ore deposit were reported by V.M. Grigor'eva, A.S. Vershinin, and others.

The Buruktal Massif is primarily composed of apoharzburgite serpentinites with apodunite serpentinite schlieren. Of particular interest is the development of a wide range of vein-facies rocks, including pyroxenites, gabbro, dolerites, diorites, spessartites, granodiorites, and plagiogmatites.

Researchers believe that weathering crust of the massif is considerably eroded. It is mainly preserved in the southern sector in the form of siliceous-ocherous and serpentinite-ocherous profiles. Consequently, ferruginous and magnesian-ferruginous ores prevail at this deposit. Serpentinites near dikes are strongly altered by talc, chlorite, and quartz. Hydrothermal-altered (talc-carbonate, listwanite, chlorite, and

**Table 4.** Characteristics of ore types from Sector 3 of the Buruktal deposit (Vershinin, 1996)

| Components, %                  | Zones               |                  | Profiles                             |                    |
|--------------------------------|---------------------|------------------|--------------------------------------|--------------------|
|                                | structureless ocher | structured ocher | leached (nontronitized) serpentinite | average content, % |
| Ni                             | 0.73                | 0.95             | 1.04                                 | 0.99*              |
| Co                             | 0.044               | 0.10             | 0.06                                 | 0.08               |
| Fe <sub>2</sub> O <sub>3</sub> | 58.10               | 34.60            | 20.40                                | 33.10              |
| Al <sub>2</sub> O <sub>3</sub> | 5.53                | 5.30             | 6.80                                 | 5.90               |
| SiO <sub>2</sub>               | 18.40               | 39.0             | 44.80                                | 39.30              |
| MgO                            | 1.51                | 5.20             | 13.40                                | 8.70               |
| Thickness of zone              | 2.0 m               | 6.6 m            | 6.8 m                                | 16.1 m             |

Note: The average Ni content (0.64%) in ores from the Buruktal deposit is based on (Proshin and Gorelov, 1997).

amphibolite) rocks, which often contain commercial concentrations of Ni, are also encountered along brecciated and schistosed zones that separate the massif into blocks. The ore potential of deep zones has not been investigated.

According to Grigor'eva and Sheshukova (1969), the weathering crust in one representative sector of the Buruktal deposit is characterized by the following features: the Ni-bearing crust occupies an area of  $2.5 \times 0.5$  km; the average orebody thickness is 16 m; and the average Ni and Co contents are 0.95 and 0.11%, respectively. Proportions of ferruginous and magnesian ore varieties are almost equal (Table 4). The typical section is as follows (from top to bottom):

The **deluvial-eluvial zone** consists of ocherous-sandy sediments with gypsum, birbrite fragments, and quartz pebbles. The Ni concentration is highly irregular and locally reaches 1.0–1.5%. The Co concentration (0.08%) is commercially significant for the Buruktal deposit. The thickness of the zone ranges from 1 to 4 m.

The **structureless (friable) ocher zone** comprises goethite, hydrogoethite, gel-type halloysite, along with hypergene magnetite and chrome spinel grains. Thickness 1–3 m.

The **structured ocher zone** consists of brownish red, banded or spotty, massive rocks with a relic schistosed structure of underlying nontronites. The mineral composition is as follows (%): goethite and hydrogoethite 40–50, hematite and hydrohematite 5–10, hypergene magnetite 6–12, talc and serpentine 1–10, nontronite 2–8, quartz, opal, and chalcedony 10–20, manganese hydroxides (including asbolanes) 3–5, halloysite and ferrohallysite 5–7, chrome spinels 0.5–5, and relic magnetite 2–5. Unlike the relic magnetite, the hypergene fibrous variety is observed as accretions with hematite and hydrohematite. Asbolanes make up stringers, colloform patches, and dendrites. Siliceous minerals are observed as stringers and ferruginous concretions (birbirites) up to 20 cm across. The occasional nodules and interlayers of chrysoprase and prasopall contain as much as 0.5–3.5% NiO.

The major Ni-bearing mineral is represented by the cryptocrystalline hydrogoethite with a colloidal admixture of nickel hydroxide (NiO 0.5–3.6%). Nickel is partly contained in nontronite (0.5–2.3%) and manganese hydroxides (1–6%). Cobalt is concentrated in hydrogoethite (up to 0.1–0.35% in some varieties), manganese hydroxides (0.4–5.0%), and hypergene magnetite (0.1–0.23%). Total thickness is 2–10 m (up to 25 m in pockets).

The **nontronitized serpentine zone** is composed of the following minerals (%): antigorite, bastite, and nontronite (50–65); montmorillonite, chrysotile, kerolite, serphophite, talc, and chlorite (up to 10); iron and manganese hydroxides, along with hypergene magnetite 15–25; chrome spinels and relic magnetite 10; and opal, chalcedony, and quartz 2–4. Nickel is primarily concentrated in nontronite (Ni 1.2–1.8%), iron minerals (Ni 0.4–3.4%), chlorite, and manganese hydroxides. Cobalt is concentrated in manganese hydroxides (asbolanes), hydrogoethite, and hypergene magnetite. In the upper section, at the contact with overlying structured ochers, one can sometimes observe thick (0.3–1.0 m), almost nontronite-only lenses. Total thickness is 1.0–3.5 m (locally up to 9 m).

The **leached serpentinite zone** consists of greenish gray, retiform serpentinite with stringers of opal, chalcedony, quartz, carbonates, and Ni-kerolite. Major components are represented by antigorite, chrysotile, and bastite, while serphophite, nontronite, kerolite, and asbolanes are subordinate. Additionally, dike and fracture zones include Ni-bearing chlorites in the form of jefferisite (Ni 0.46–2.2%) and schuchardite (Ni 5.4–13.1%).

Nickel replaces Mg and Fe in the crystalline lattice of chlorites. However, the major portion of Ni is contained in kerolite, antigorite, and chlorites. Cobalt is concentrated in manganese hydroxides (asbolanes).

## DEPOSITS OF THE SAKHARIN MASSIF

The Sakharin Massif is located 50 km to the south-east of Magnitogorsk and confined to a deep fracture zone separating the East Uralian Uplift (Anticlinorium) from the Magnitogorsk Megasyntlinorium. The massif represents a submeridional body (length 18.5 km, average width 6.3 km) embedded within Silurian, Middle Devonian, and Lower Carboniferous volcanosedimentary rocks. It is composed of basic, ultrabasic, and alkaline basic (primarily gabbroid) rocks.

Ultrabasic rocks are generally developed in the eastern central sector in the form of a dunite core (approximately 5 km<sup>2</sup> in size) with the Sakharin deposit. The dunite core, which consists of serpentinitized dunitites, peridotites, and wehrlites, is crosscut by numerous dikes and veins of the predominant gabbro series. Near the contact with dikes, dunitites are commonly transformed into often schistosed antigorite rocks (Borodina *et al.*, 1974). Eluvium of plagioclase pyroxenites, frequently developed in the dunite–gabbro contact zone, is enriched in Ni. In terms of structure and composition, the Sakharin Massif is analogous to massifs from the Uralian Platinum Belt.

The weathering crust, which is widespread on the massif, is locally covered with Paleogen–Quaternary sediments up to 10–15 m thick. The thickness of the weathering crust ranges from 10 to 20 m. However, it can increase up to 100 m in pockets at contacts with dikes.

The generalized profile of the Ni-bearing weathering crust is as follows (from top to bottom):

The **ocherous and ocherous–siliceous zone** (depth interval 1.0–25 m) is composed of a yellow or dark brown, primarily friable (less commonly, indurated) substance. The indurated variety is characterized by a relic serpentine texture (the so-called structured ocher). Attention is drawn to the fact that rocks of this zone are enriched in Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, Mn, and Cr. According to petrographic study carried out by K.F. Samarina and F.A. Sysoev (Vtorushin and Zhuravleva, 1972), ochers consist of the predominant goethite and hydrogoethite (>50%), the secondary halloysite and kaolinite (10–15%), the less common quartz, chalcedony, and opal (5–15%), and the rare chlorite, magnesite, calcite, antigorite, hematite, chrome spinels, asbolanes, and magnetite. Nickel is mainly concentrated in goethite and hydrogoethite.

The **nontronite and nontronitized serpentinite zone** (depth interval ranging from 1–2 to 20–25 m) is generally represented by highly indurated, nontronitized, and often ocherous serpentinites. Pure nontronites are only encountered as separate greenish lenses. The elevated Al<sub>2</sub>O<sub>3</sub> content (as much as 4–6%) in them is related to the admixture of montmorillonite, chlorite, and halloysite. Nickel is mainly concentrated in nontronite, chlorite, and goethite, while Co is accumulated in asbolanes.

The **leached serpentinite zone** consists of highly porous, locally silicified, whitish or greenish gray rocks grading into disintegrated serpentinites. The mineral composition is as follows (%): serpentine (30–50), nontronite, kerolite, and montmorillonite (20–30), chlorite (up to 12), quartz, chalcedony, and opal (up to 15), and goethite and hydrogoethite (5–10). The minor components are represented by chrome spinels, asbolanes, manganese hydroxides, talc, calcite, and magnesite.

The **disintegrated serpentinite zone** comprises massive, locally fractured, dark gray or greenish gray serpentinites. Major minerals are represented by antigorite, chrysotile, lizardite, olivine, magnetite, and chrome spinels. Additionally, serpophite, magnesite, quartz, and opal are found in stringers. The ore-bearing area of the section lacks nickel minerals, such as garnierite and revdinskite (nepouite) that are typical of thermal hypergenesis deposits.

The problem of platinoids in weathering crusts of ultrabasic rocks in the Urals was recently scrutinized by a team of geologists at the St. Petersburg Mining Institute under the supervision of Prof. V.G. Lazarenkov (see works of Yu.A. Volchenko, N.I. Vorontsova, V.G. Lazarenkov, and I.V. Talovina). Results obtained by these researchers suggest that Ni-bearing weathering crusts at the Sakharin and other deposits of the Ural region are characterized by elevated (sometimes commercial-grade) concentrations of platinum group elements, particularly Pt and Pd (Talovina, 1997).

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The first nickel prospecting and exploration works, carried out in 1960–1964, revealed eight Ni-bearing sectors of the Serov deposit. The Elov sector, which is assigned to the eastern margin of the Kola Massif and geographically confined to the western slope of the Sos'va Depression, was identified as the most prospective sector. The depression is infilled with Jurassic, Cretaceous, Paleogene, and Quaternary sediments. Serpentinites within the Elov sector are hydrated and replaced by chamosite. The altered serpentinites are successively overlain by Paleogene clayey opokas and Quaternary sandy loams (Fig. 3).

The study and interpretation of results of prospecting works in this district continued during the 1960s (see works of E.N. Kuzemkina, V.M. Grigor'eva, K.G. Borodina, L.I. Kononova, N.A. Zhuravleva, and others). The openpit mining of the Elov sector was started at the end of 1980s. By 1994, the openpit reached a depth of 40 m. In 1996, taking into consideration reports of the Vorontsov geological team, Prof.

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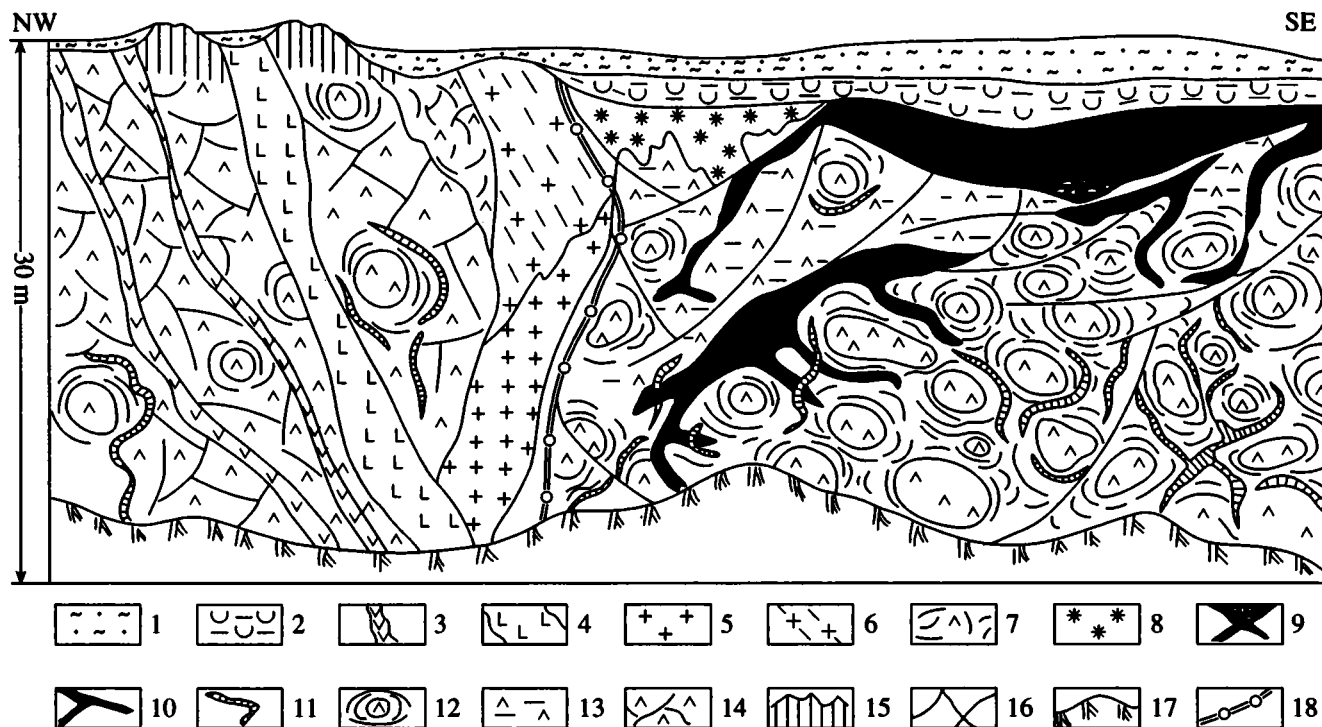


Fig. 3. Schematic drawing of the northeastern wall of the Elov openpit, Kola Massif, Serov ore district (as of July, 1994). (1) Quaternary sandy loam; (2) Paleogene clayey opoka; (3) diabase veins; (4) pyroxenite dike; (5) diorite dike; (6) montmorillonite-kaolinite eluvium of the diorite dike; (7) nontronite with local relics of serpentinite texture; (8) dark red massive ocher; (9) black chamosite claystone with inclusions of chamosite-altered serpentinite (leached serpentinite rubble in some places); (10) resinous black stringers and lenticular inclusions of Ni-bearing chamosite; (11) interlayers of hydrosilicates with different Ni contents (garnierite, kero-lite, sungulite, revdinskite, serpopphite, and others); (12) intensely hydrated serpentinite with nucleus structure; (13) hydrated serpentinite with talc and carbonate patches; (14) disintegrated kerolitized serpentinite; (15) silicified and leached serpentinite often accompanied with fine calcite stringers (eroded relic of the Aptian-Albian weathering crust with Cr-limonite); (16) slip deformation planes; (17) talus; (18) western boundary of the thermal window.

A.S. Vershinin from the Ural Mining Institute compiled an overview of literature data on nickel mineralization in the Serov deposit area (Vershinin, 1996).

According to the concept shared by almost all investigators of drillcore data, the Serov deposit is confined to a subaerial Triassic-Jurassic weathering crust. In Late Jurassic and Early Cretaceous, weathering crust products were altered by infiltrational-metasomatic processes and transformed into atypical (for weathering crusts in subaerial conditions) new mineral and rock assemblages, e.g., chamosite rocks containing a certain amount of relic minerals from the residual (Triassic-Early Jurassic) crust and newly formed (Middle Jurassic-Early Cretaceous) minerals, such as magnetite, siderite, manganosiderite, millerite, and marcasite (Kononova *et al.*, 1974, p. 163).

The Elov sector substrate, which hosts the major portion of explored ores, is characterized by a highly intricate geological setting. Serpentinites are ubiquitously crosscut by dikes and veins of diverse (in composition and age) rocks. All rocks, except Jurassic (or even Early Cretaceous) dolerites and pyroxenites from dikes in the northwestern sector of the openpit (Fig. 3), are intensely crushed, brecciated, and often schistosed.

Based on borehole data and our observations, the rocks are significantly fractured and crosscut by submeridional and sublatitudinal displacements. Stringers of various nickel hydrosilicates are developed along all displacements over the exploration depth interval (60–150 m). The base of several boreholes is significantly mineralized and contains as much as 0.6–0.8% Ni.

The weathering crust of the Elov sector can be divided into the lower (residual) and upper (infiltrational-metasomatic) zones. Commercial Ni concentrations are ubiquitous in the weathering crust. Nevertheless, the mineralization is most widespread and maximal in the upper (altered) crust that embraces the ore-bearing column of the section.

Results of our work at the openpit in 1994 casted some doubt upon the validity of the currently popular notion concerning the genesis of orebodies in the Serov deposit.

First and foremost, we should emphasize the following fact. The isometric or slightly extended orebodies at the Elov openpit are confined to most altered sectors of the serpentinite massif. Slightly altered and locally unaltered serpentinites are exposed at a distance of mere 50–100 m from the openpit. In works devoted to



**Table 5.** Chemical composition of Ni-bearing silicates from the Serov deposit

| Nos. | Minerals                               | Chemical composition |                                |                                |       |       |       |                               |                               |      |
|------|----------------------------------------|----------------------|--------------------------------|--------------------------------|-------|-------|-------|-------------------------------|-------------------------------|------|
|      |                                        | SiO <sub>2</sub>     | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | FeO   | MgO   | NiO   | H <sub>2</sub> O <sup>+</sup> | H <sub>2</sub> O <sup>-</sup> | Co   |
| 1    | Chlorite                               | 18.90                | 20.20                          | 10.05                          | 31.90 | 3.43  | 2.05  | n.a.                          | n.a.                          | n.a. |
| 2    | The same                               | 25.40                | 11.70                          | 15.73                          | 24.81 | 7.56  | 1.30  | n.a.                          | n.a.                          | n.a. |
| 3    | Sungulite (chlorite-type)              | 40.15                | 1.63                           | 0.57                           | 2.37  | 29.39 | 13.50 | 11.85                         | 1.23                          | n.a. |
| 4    | The same                               | 38.75                | 2.70                           | 2.00                           | 0.71  | 26.46 | 15.53 | 11.08                         | 1.98                          | n.a. |
| 5    | Hydrogoethit                           | 4.30                 | Traces                         | 81.06                          | 1.43  | 0.28  | 1.16  | 11.43                         | n.a.                          | n.a. |
| 6    | Chamosite (infiltrational-metasomatic) | 20.48                | 14.66                          | 15.41                          | 33.89 | 0.88  | 2.08  | 10.40                         | 0.32                          | 0.53 |
| 7    | The same                               | 25.00                | 12.98                          | 15.71                          | 19.42 | 9.58  | 1.71  | 10.91                         | 1.62                          | 0.52 |
| 8    | Serpophite stringers                   | 48.59                | 0.31                           | 1.17                           | n.a.  | 33.97 | 5.69  | n.a.                          | n.a.                          | n.a. |
| 9    | Ocherous-chamosite (sedimentary) rock  | 35.79                | 6.04                           | 21.38                          | 16.99 | 9.52  | 1.38  | n.a.                          | n.a.                          | n.a. |
| 10   | Chamosite-ocherous rock                | 31.15                | 3.78                           | 33.92                          | 3.02  | 1.75  | 0.90  | n.a.                          | n.a.                          | n.a. |

Note: (nos. 1–5) based on Grigor'eva (1969); (6, 7) based on Kuzemkina (1970); (8–10) based on Mikhailov (1998). (n.a.) not analyzed.

the Serov deposit, the lack of eluvium is explained in the following way: "the ancient weathering crust, which was obviously very thick during the Triassic–Jurassic time, was preserved as patches in crystalline rocks, including serpentinites" (Grigor'eva, 1967, p. 273). If so, where did the weathering crust disappear? The overlying Jurassic and Lower Cretaceous sediments bear no signs of the redeposition of a very thick Ni-bearing eluvium. In contrast, substrate derivatives at the base of sedimentary lenses include feldspar fragments, along with chlorite and mica flakes (Fig. 3), i.e., mineral assemblages that are incoherent for the chemically well-processed eluvium.

The Aptian–Albian (Cr- and Ni-bearing) limestone, which unconformably overlies the Triassic–Lower Cretaceous sedimentary sequence, is a different matter. It represents redeposition products of the widespread (in the Urals) Aptian–Albian weathering crust and has nothing to do with Ni-bearing chamosite rocks that are related to thermal hypergenesis and restricted to thermal windows of the Early Mesozoic tectonomagmatic activation.

The first thing, which attracts our attention, is the distinct boundary between eastern and western sectors of the openpit (Fig. 3). The right-hand (eastern) wall presumably represents a section of the central thermal window that was most intensely altered by Ni-bearing hydrothermal solutions. This sector is profusely decorated with an increasing-upsection number of veins and interlayers of resinous black claystones. In several cases, the claystones make up lenses on the surface of altered serpentinites and, in turn, are discordantly overlain by Paleogene clayey opokas. The base of obviously sedimentary lenses infrequently contains leached serpentinite detritus (rubble and fine gravel), quartz and feldspar grains, chlorite (bright green variety) and mica grains, along with rare plant tissue fragments. The entire exposed section of the lense at the openpit is

impregnated with fine orthorhombic crystals of siderite. In the dry state, the apparently resinous-black organic matter turns into a whitish gray substance composed of the colloform Ni-bearing chamosite (Table 5). Additionally, it is pertinent to note that even the uppermost portions of orebodies are characterized by high contents of Fe and Mg.

The eastern, chamosite-bearing wall of the openpit comprises leached and metasomatically altered serpentinites with a nucleus structure. The nucleus size varies from 5–10 cm to 1–2 m. The central portion of the nucleus generally consists of greenish gray serpentinite and is enveloped with a reddish brown shell of the same serpentinite, which is slightly altered by talc and carbonates. The next, dark gray shell is composed of a more altered variety of serpentinite with newly formed chlorite, kerolite, talc, and carbonate inclusions. The Ni content is commonly up to 0.5–0.6% in the central nucleus and as much as 1–2% in shells. The internucleus space often hosts stringers of a rather massive, colloform substance consisting of various Ni-bearing hydrosilicates, such as kerolite, sungulite, serpophite, garnierite, and others. The Ni content in these minerals is generally as high as 10–15% (Table 5).

The geological section is quite different in the western sector located behind a moderately thick granodiorite dike, which terminates the thermal window. Black chamosite rocks are practically absent. The substrate hydrolysis is appreciably weaker. Serpentinites in the uppermost section of the substrate (under the Quaternary sedimentary cover) underwent an intense quartzification and carbonatization (Fig. 3). Near the contact with thermal window, the granodiorite dike is weathered. Its upper section is kaolinized. A pocket of goethite–hydrogoethite ocher is developed adjacent to the window. In other words, the western sector is characterized by the development of a profile that is typical for Cretaceous subaerial weathering crusts.

Millerite, a ubiquitous mineral at the Serov deposit, is represented by two generations (Kuzemkina, 1970a, p. 213). Millerite 1 occurs at the base of sections unaltered by superimposed processes. It is associated with the hydrothermal serpophite and carbonate minerals in slightly altered and disintegrated serpentinites. Garnierite spherulites are found in similar conditions. Millerite 2 is encountered in the uppermost section in chamosite and ocherous rocks. It is associated with siderite and pyrite.

Observations at the Elov openpit and laboratory analyses of rock samples indicate that the exposed sector represents the upper section of an ore stock, which is related to thermal hypergenesis and genetically similar to nickel ore stocks from the Ufalei ore district (Mikhailov, 1997) rather than a Ni-bearing weathering crust or surficial hypergene body (*Prognoznaya ...*, 1998). In other words, the Elov orebody represents the uppermost section of a Ni-bearing hydrothermal system that existed during the Early Mesozoic tectonomagmatic activation on the eastern slope of the Urals.

Under the influence of thermal, reductive, hydrocarbonate (gleyey) solutions ascending along intensely crushed rocks (serpentine melange) in the deep fracture zone, serpentinites were subjected to hydrolysis, resulting in the formation of a specific mineral assemblage of Ni-rich serpophite, chamosite, chlorite, millerite, talc, nickel hydrosilicates (garnierite and others), and carbonates. Locally, ore-bearing hydrothermal solutions effused on the surface, producing peculiar fumarole basins without organic matter. The sediments were enriched in Ni owing to the percolation of hydrothermal waters through the ultrabasic massif.

Our model of high-grade nickel ore deposition in the weathering crust at the Serov deposit resolves the problem of Ni source, which was attributed by proponents of the eluvial hypothesis to mud waters enriched in Ni and organic matter. The most essential advantage of our hypothesis resides in the fact that it proposes prospecting guides for high-grade nickel ore deposits in the hypergene zone of the Urals (Mikhailov, 1997).

#### *Infiltrational-Sedimentary Ores*

Nickel is among the few elements that do not make up autonomous sedimentary ore deposits. This unique feature is primarily related to the low mechanical strength of all of its hypergene minerals. During the epigenesis, nickel is only absorbed by organic matter and hydroxides of Mn and Fe. In the Urals, this process could develop near or within Ni-bearing massifs. Autonomous sedimentary (or sedimentary-metasomatic) nickel ore deposits are unknown in the Urals.

The Ni sorption on organic matter can be exemplified by the occurrence of kersinites, i.e., lignite clays with a commercial Ni content, in the Ufalei district. This rock, discovered as early as the beginning of the 20th century, has the following chemical composition

(%): water 7.76, ash 13.91, carbon 41.12, hydrogen 4.05, oxygen 29.13, and traces of CO<sub>2</sub>, N, S, and SO<sub>3</sub>. The ash is composed of the following components (%): NiO 15.64, CaO 0.98, and Cr<sub>2</sub>O<sub>3</sub> 1.66 (Glazkovskii, 1936).

Of specific interest is the unconventional Novyi Aidyrlyn deposit discovered during World War II. It is associated with the Aidyrlyn Massif located 120 km to the southeast of Orsk. In terms of tectonics, it is practically confined to a deep fault in the East Uralian Uplift area (Fig. 1). The massif is thrust over Lower Carboniferous coaliferous shales with limestones. The thrust zone is marked by an erosional karst valley infilled with Cretaceous and Paleogene continental sediments. We suppose that the exhausted isometric deposit was associated with a thermal hypergene stock that originated during the Early Mesozoic tectonomagmatic activation. Ores were represented by quite large, separate lenses of massive sulfides (millerite, pyrite, and marcasite with a high Ni content). The orebody was selectively mined immediately after the discovery. Several well-known geologists studied this deposit; however, their genetic concepts were irreconcilable. D.V. Nalivkin, I.I. Ginzburg, and others assumed that millerite-rich ores were accumulated in H<sub>2</sub>S-contaminated lakes and bogs. V.N. Razumova, N.P. Kheraskov, and others were proponents of the hydrothermal genesis with a partial redeposition of sulfides in the Tertiary time. Geological works were not carried out at this deposit after the war period.

#### CONCLUSIONS

The Ural region incorporates numerous nickel ore deposits and occurrences that make up a common genetic series, in which all members are related to ultrabasic massifs of the dunite-harzburgite association. The genetic series is represented by endogenic ores (sulfides), exogenic ores (oxides and silicates related to thermal hypergenesis and weathering crust), and infiltrational-sedimentary ores (sulfides, oxides, and silicates).

Currently, based on the approval of the State Reserve Committee of the Russian Federation, only oxide-silicate ores of the weathering crust with a rather low Ni content (0.7–1.1%) are mined. The exploitation of such ores was possible under conditions of the socialistic planned economy and heavy state subsidies. However, since Russia has entered the market economy system, nickel plants of the Urals have become non-competitive, and nickel production in the Urals is declining. Due to the lack of high-quality raw minerals, presently only 20 to 30% capacity of nickel plants is used in this region. Nevertheless, officials of the Ministry of Natural Resources continue to affirm that probable nickel resources in the Urals amount to millions of tons. Moreover, according to some members of the Russian Academy of Sciences, nickel reserves (not mineragenic potential or prognostic resources) suitable

for the commercial exploitation in present-day conditions are estimated at several millions of tons.

In the recently published book of Ovchinnikov (1998), for instance, one can see detailed tables showing metal reserves and contents at numerous nickel ore deposits in the Urals. According to Table 2 in this book, the sum total of nickel reserves turns out to be approximately 3 Mt, i.e., more than the reserves in Indonesia, one of the major exporters of nickel ore in the world. Moreover, Ovchinnikov points out the Ufalei group deposits with nickel reserve of  $720 \times 10^3$  t with an average Ni content of 1.2–1.6% and the Buruktal deposit with nickel reserve of  $1377 \times 10^3$  t, the average Ni-adjusted, i.e., (Ni + 6 Co), content being equal to 1.33%. According to this researcher, other 113 nickel ore deposits in the Urals also have similar attractive characteristics.

Estimates of Ovchinnikov can only be qualified as an annoying mistake of a scientist who is unfamiliar with the real state of affairs. Actually, orebodies with Ni content >1% have been exhausted in the Ufalei group deposits located near the nickel plant. The Elov openpit (Serov deposit) situated 500 km to the north of the Ufalei Plant has long been the main supplier of ores with an average Ni content of 1.1–1.2%. The Yuzhuralnikel Plant is operating on the basis of ores from the Buruktal deposit located at a distance of 200 km. The Ni content in these ores is 0.64% (Proshin and Gorelov, 1997). The processing of such low-grade ores can hardly be feasible, unless the technology of their comprehensive processing with the maximal extraction of Co, associated iron minerals, and Pt is used.

The analysis of available data on the nickel potential of the Ural region demonstrates that commercial nickel ores complying with requirements of the modern industry were only generated in polychronous and polyfacies deposits where endogenic (or thermal-hypergene) and eluvial ores are superposed. We assume that such deposits can be discovered in the serpentinite melange of the Uralian MTZ and other deep faults from either side of the eastern Urals and Transural Uplift areas that surround the Tagil–Magnitogorsk Trough. The prospecting for these nickel ore deposits can require a significant capital investment.

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# Lithological and Hydrogeochemical Role of the Density Convection in Sedimentation Basins with Halogenous Formations

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**Abstract**—This work treats lithofacies and hydrogeochemical features of the Late Paleozoic sedimentation on the eastern Russian Plate and the geochemistry of principal types of brines, which are spatially and genetically related to halogenous formations. It is shown that the density convection of primary magnesian chloride brines, which inflow into underlying Paleozoic and Proterozoic rocks from Permian evaporite paleobasins, plays the principal role in the formation of chlorocalcium brines that are predominant in the sedimentary cover of the Volga–Urals sedimentation basin. The problem of metamorphization of brines by exchange-adsorption and hydrolytic processes in terrigenous rocks and the problem of metasomatic dolomitization of limestones are discussed.

In the underground hydrosphere, which is subjected to actions of various geophysical fields, the mass transfer in the water–rock–gas–organic matter system is carried out with the help of diffusion and convection related to gradients of substance concentration, pressure, and temperature. Molecular-diffusion processes including pressure diffusion, thermal diffusion, self-diffusion, and concentration diffusion are characteristic of hydrodynamically passive media, which correspond with the zones of the very difficult water exchange and quasi-stagnant regime at the depths of over 1.0–1.5 km in the platform-type sedimentary basins. Geochemically, the most significant process is the concentration diffusion occurring in the solution or on the interface between solid and liquid phases due to the difference in the substance concentration. The result of this diffusion is the equalizing of the solute concentration in the underground hydrosphere in the course of geological evolution. Thus, lithological and hydrogeochemical systems tend to the state of thermodynamic equilibria. Filtration (forced convection) plays the principal role in the transfer of solute together with solvent in the upper hydrogeodynamic zones of sedimentary basins characterized by high rock permeability, pressure gradient, and groundwater flow rate.

A natural (free or density) convection is a heat and mass transfer in the Earth's gravity field due to gradients of temperature and concentration causing a difference in the density of groundwaters.

Thermal convection appears in the form of the warm light flows breaking through the medium of cooler heavy waters. The necessary condition of realization of this process (in addition to the significant temperature gradient) is the high permeability of geological formations (faults, karstogenic zones, and others). Therefore,

the role of thermal convection in the mass transfer is local.

Unlike the thermal convection, the concentration convection in the specific paleohydrogeological and lithohydrogeochemical conditions can control the formation of deep-seated groundwater. Experimental studies (Valyashko *et al.*, 1965; Polivanova, 1982) have shown that the aquiferous system consisting of heavy liquid in its upper part and light liquid in its lower part is unstable in the Earth's gravity field. Due to the gradient of the water density, the gravity jet stream movement is induced: the heavy solution descends downward, and the light one ascends upward. It was established that the convection occurs mainly in the form of separate, slightly mixed streams. The submergence–emergence process for waters with different density ( $\rho = 1.0\text{--}1.5\text{ g/cm}^3$ ) is close to the isochoric one; i.e., it is not accompanied by variation in volume and is completed when solutions are distributed by densities (heavy solutions will be on the bottom; and light ones, on the top).

Gravity submergence of brines takes place both in well-permeable rocks and in clays. In the latter case, the heavy solution moves not only along the fracture zones of clay, but also through its pores and along fissures, which are formed under the action of brines. A specific feature of the density convection is the formation of peculiar brine cones opening from the accumulation centers (in natural conditions, from the bottom of the halogenous basin).

The density convection rate  $V_\rho$  is described by equation

$$V_\rho = K_z I_\rho / n_0,$$

where  $K_z$  is the coefficient of rock filtration in the vertical direction;  $I_\rho$  is the vertical gradient of the density convection; and  $n_0$  is the active rock porosity. The value  $I_\rho$  is determined by relationship  $I_\rho = \rho_1 - \rho_2/\rho_2$  ( $\rho_1$  and  $\rho_2$  are densities of heavy and light liquids, respectively).

Thus, the principal parameters determining the intensity of gravity submergence of the heavy solution are the permeability of geological medium and the value of vertical gradient of convection. In nature, the formation of conditions favorable for the mass exchange through the density convection mechanism takes place, when halogenous basins are formed on the surface, with the liquid phase represented by primary heavy brines. In the Earth's history, such brines existed during the Late Proterozoic (Iran-Pakistan Basin), Paleozoic (East Siberian, Pre-Appalachian, Dnieper-Donets and other basins), Mesozoic (North European, North Caucasian, Central Asian and other basins), and Cenozoic (Rheinian, Cis-Carpathian, Mesopotamian, and other basins). However, the halogenesis was most extensive and intense in the Permian period, when the two largest halogenous basins (Central European and East European basins) were located on the territory of Europe, with an area over  $2 \times 10^6$  km<sup>2</sup> (Zharkov, 1974; Merzlyakov, 1979).

The object of these studies is the central part of the East European Basin, which geotectonically corresponds to the Volga-Urals Antecline and adjacent part of Cis-Urals Foredeep. In the regional hydrogeology, this territory is known as Volga-Urals artesian basin. Within this basin, the Archean basement lies at the depth ranging from 1–2 km on the arch uplifts (Tatar, Tokmov, Zhiguli-Pugachev and other uplifts) to 5–8 km or more in basins (Verkhnyaya Kama, Solikamsk, Bel'sk, and other basins). The cover of the basin is composed of Late Proterozoic and Phanerozoic sediments; however, on the greater part of the region, the Paleozoic rocks play the major role.

Continental and marine terrigenous-carbonate sediments fill deep (up to 4.5–8.5 km) aulacogens surrounding the Volga-Urals antecline in the east. The hydrogeological history of this long-term eon (about 1 Ga) is still very poorly studied. It should be assumed that the Riphean and Vendian sedimentation basins were periodically subjected to slight salinization, fixed by the occurrence of dolomites and terrigenous, red-colored sediments. At the same time, three prolonged regional hiatuses were observed in the Late Proterozoic and Early Paleozoic, when the territory was subjected to dessication, and the infiltration waters penetrated into the upper part of the exposed oldest formations.

During most parts of the Paleozoic era, the sedimentation occurred under conditions of sea basins with normal and increased salinity. The thick strata of the Devonian, Carboniferous, and Lower Permian carbonate rocks are related to these basins, occupying up to 80–90% of the whole Paleozoic sequence. Evaporites

(dolomites and, rarely, gypsum), which serve as indicators of the existence of salinized sea basins, are found in various stratigraphic subdivisions of the Paleozoic (Frasnian and Famennian stages of the Upper Devonian, Visean and Moscovian stages of the Middle Carboniferous, Gzhelian Stage of the Upper Carboniferous) and in various parts of the territory.

Compared to stages of the elision regime, in the pre-Early Permian history of the Volga-Urals Basin evolution, the infiltration stages corresponding to continental hiatuses played a subordinate role (early Eifelian, late Givetian, early Visean, late Namurian, and Vereyian times), with the depth of infiltration water penetration being less than a few hundred meters. On the whole, the paleohydrogeological environment favored the accumulation and conservation of normal marine and brackish waters.

However, a large mass of brines contained in Paleozoic and Riphean-Vendian sequences was governed by the Early Permian and, partially, Late Permian halogenesis that terminated the elision stage. The elisional process started in the Moscovian (Middle Carboniferous) and ended in the Tatarian (Late Permian). The total thickness of the Permian sequence increases from 200–300 m in the west of the region to 2000–2500 m in the east. Halogenous rocks occur at various levels of the Permian sequence.

The Asselian, Sakmarian, and Artinian stages have a similar lithofacies composition and common distribution pattern of rocks. In plan, the Asselian-Artinskian facies rocks are traced in the form of submeridional bands along the Urals: the western sector of the basin incorporates dolomite-anhydrite rocks corresponding to the most salinized part of the epicontinental sea basin; to the east, they are replaced by sulfate-dolomite, dolomite-limestone, and limestone assemblages. In the easternmost (Cis-Urals) sector, the mollassic sediments (sandstones, mudstones, conglomerates) representing the disintegration product of Urals Fold-belt rocks are widespread.

The Kungurian Age was marked by a slight reduction and considerable shallowing of the evaporitic basin even in the region of the Cis-Urals Foredeep. In this basin, under conditions of arid climate and permanent subsidence of the basin bottom as a result of tectonic subsidences, gypsum, rock salt, and potassium and magnesium salts were deposited due to a progressive concentration of seawater, marking the respective stages of halogenesis. The dolomite-gypsum facies is most widespread, occupying about 75% of the Volga-Urals Antecline. The rock salt sequence was accumulated in its southern part, while the halite-sylvinite sequence (thickness 1500–2000 m) was accumulated in the adjacent regions of the Bel'sk Depression of the Cis-Urals Foredeep. In the Solikamsk Depression of the foredeep, carnallite was precipitated together with halite and sylvinite due to a concentration of primary brine. The total thickness of halogenous horizons

amounts up to 800–900 m in the central part of this structure and is reduced to 400–500 m on its periphery.

To the south of the Volga–Urals Antecline, on the territory of the Caspian Depression, the thickness of the salt rocks amounts to 5–8 km and more. Halite–sylvinite and carnallite–bischofite rocks play a significant role in its composition.

The Kazanian Stage is characterized by thick (up to 200–300 m) strata of evaporites (anhydrites, salts) in southern regions of the Volga–Urals Antecline (Buzuluk Depression). On the rest of the region, it consists of sulfate–carbonate and carbonate–terrigenous complexes.

Thus, hydrochemical conditions were not constant in time and space, which predetermined the diversity of accumulated evaporites. At the same time, this is a typical marine paragenesis of chemogenic minerals and rocks (limestone, gypsum, halite, epsomite, sylvinite, carnallite, bischofite); therefore, it is quite competent to use data on the artificial concentration of seawater (Valyashko, 1962; Zhrebtsova, Volkova, 1966). This concentration is accompanied by successive precipitation of the following salts (g/l):  $\text{CaCO}_3$  (at solution concentration of 15–36),  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (135–150),  $\text{NaCl}$  (320),  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  (430),  $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  (470), and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  (510). Simultaneously, the seawater is metamorphized: sodium chloride water is transformed into the magnesium chloride one. With an increase in the solution concentration, its density increases from 1.025 g/cm<sup>3</sup> (normal seawater) to the following values corresponding to the initial stage of the precipitation of relevant minerals (g/cm<sup>3</sup>): 1.131 (gypsum), 1.227 (halite), 1.290 (sylvite), 1.318 (carnallite), and 1.367 (eutonic stage, when bischofite is precipitated) (Fig. 1).

Chloride brines of the Volga–Urals Basin, which are spatially and genetically related to the Permian halogenous formations, are represented by three principal geochemical types: (1) Mg- and Na–Mg-brines (230–475 g/l); (2) Na-brines (36–320 g/l); and (3) Na–Ca and Ca–Na-brines (200–330 g/l).

Magnesium chloride (intra- and intersalt) brines were studied in Solikamsk, Buzuluk, and Caspian depressions, where they fill pores and fissures in Permian salts, as well as carbonate and clayey interlayers and lenses at the depth of 400–1500 m and more. They contain very high concentrations of Mg (up to 80–110 g/l), Br (17.5), K (42), B (1.2), Sr (3.5), Rb (0.1), Li (0.05), Cs (0.001) and relatively low concentrations of I (0.005–0.02 g/l). The typical geochemical parameters are as follows:  $r\text{Na}/r\text{Cl} = 0.11\text{--}0.64$ ,  $\text{Cl}/\text{Br} = 15\text{--}71$ , and  $r\text{SO}_4 \times 100/r\text{Cl}$  ranges from 0.05 (Solikamsk Depression) to 1.5–3 (Buzuluk and Caspian depressions). The Ca content is low (less than 10–20%),  $r\text{Mg}/r\text{Ca} = 10\text{--}360$ . Water-dissolved gases are represented by nitrogen and methane. These highly concentrated brines represent the slightly altered primary brine

corresponding to the last stages of seawater concentration (halite, epsomite, and carnallite stages).

The sodium chloride type include brines of the Permian and Carboniferous super- and subsalt sediments. These brines occur up to the depth of 1000–1500 m in the low water exchange zone. They are characterized by low-grade metamorphism ( $r\text{Na}/r\text{Cl} = 0.9\text{--}1.0$ ), the depletion in Br (<0.2 g/l,  $\text{Cl}/\text{Br}$  up to 8000), I (up to 0.001–0.1 g/l), Sr (up to 0.16 g/l), and rare alkaline metals, but high contents of sulfates ( $r\text{SO}_4 \times 100/r\text{Cl} = 1\text{--}10$ ) and B (up to 0.6 g/l or more) and  $r\text{Mg}/r\text{Ca} = 0.4\text{--}3.5$ . Usually, the K concentration is low (<0.1 g/l), but in case of contact with the potassium salt, it can amount to several grams per liter. Brines contain gases of the hydrosulfide–nitrogen and hydrosulfide–carbon dioxide–methane–nitrogen composition. Genetically, these are typical leaching brines resulting from the interaction between infiltration waters and the solid (predominantly halitic) phase of halogenesis with the participation of molecular diffusion of Na and Cl from salt-bearing strata.

Sodium chloride and sodium chloride brines are the major type of waters of subsalt (deep-seated) sedimentary complexes. They form a spatially consistent hydrochemical zone, whose thickness in basement depressions ranges up to 5–7 km (up to 10 km in the south of the Cis-Urals Foredeep. The brines are confined to the Lower Carboniferous, Devonian, and Upper Proterozoic sediments, which are located in quasi-stagnant hydrogeodynamic environments. They are characterized by a high-grade metamorphism ( $r\text{Na}/r\text{Cl} = 0.1\text{--}0.7$ ,  $\text{CaCl}_2$  up to 50–80%), low sulfate content ( $r\text{SO}_4 \times 100/r\text{Cl} = 0.02\text{--}0.7$ ), enrichment in Br (up to 2.2 g/l), Sr (up to 1.2 g/l), Rb (up to 0.02 g/l), Li (up to 0.035 g/l), Cs (up to 0.001 g/l) and, on the contrary, depletion in B (<0.002 g/l), subacid medium (pH 5.9–7.0), negative Eh values (up to –300 mV), and nitrogen–methane gas composition with high concentration of He (up to 10 ml/l). Iodine concentration is usually less than 0.02 g/l, but it amounts to very high values (0.07–0.1 and, sometimes, 0.25 g/l) in brines of the Bel'sk and Solikamsk depressions. The  $\text{Cl}/\text{Br}$  and  $r\text{Mg}/r\text{Ca}$  coefficients decrease to 160–75 and 0.05, respectively.

The formation of these peculiar liquid ores, enriched in a wide range of halophile elements and rare alkaline metals, is one of the important problems of modern genetic hydrogeochemistry. This problem was discussed in works of many hydrogeologists and lithologists; however, up to the present, it is far from being solved. In our opinion, the set of natural facts is best explained by the lithogenetic conception, which attributes the formation of chlorocalcium brines to the hydrochemical evolution of waters in sedimentation basins of the past geological epochs during the halogenesis and the following processes of metamorphization of halogenous brine at the stages of diagenesis and epigenesis.



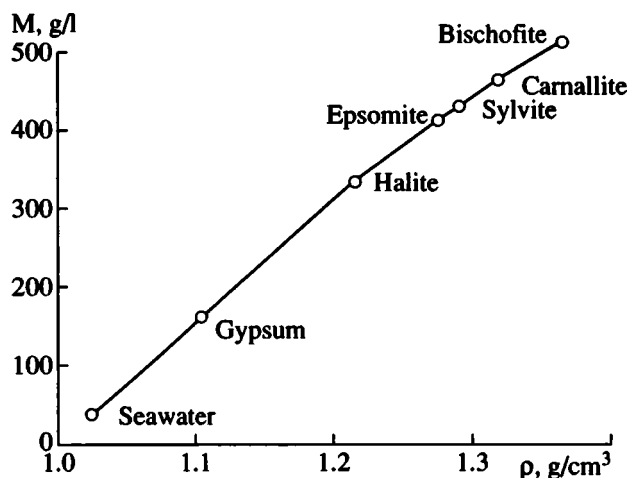


Fig. 1. Variation in mineralization and density of marine brine in the course of salt crystallization (based on data of Valyashko, 1962 and Zhrebtsova and Volkova, 1966).

Hence, the Early/Late Permian boundary in the eastern Russian Plate was marked by a gravitationally unstable hydrogeodynamic and hydrogeochemical system, with the surficial part represented by an evaporitic basin with highly mineralized (up to 400 g/l and more) primary heavy ( $\rho_1$  up to 1.3–1.37 g/cm<sup>3</sup>) magnesian brine, and the underground part was represented by the Carboniferous, Devonian, Vendian, and Riphean carbonate and, to a less degree, terrigenous rocks, saturated with the less mineralized (30–150 g/l), and, consequently, lighter ( $\rho_2 = 1.02$ –1.11 g/cm<sup>3</sup>) waters. During the preceding, long-term (>1.3 Ga) stage of evolution, the underground part of the hydrochlorosphere underwent convective-diffusion differentiation of material, which caused the segregation of hydrogeochemical zones of very dilute (up to 75 g/l) and dilute (up to 150 g/l) brines.

The vertical gradient of the concentration convection  $I_p$  varied within a wide range, depending on the ratio between densities of the surface brines of the Permian evaporitic basins and the underlying brines in the Paleozoic and Proterozoic sediments. Judging from lithohydrogeochemical data, the Permian environment was characterized by a gravitational subsidence of the gypsum stage brines ( $\rho_1 = 1.13$ –1.23 g/cm<sup>3</sup>) into the medium of dilute brines ( $\rho_2 = 1.05$ –1.13 g/cm<sup>3</sup>). In this case, value  $I_p$  is 0.08–0.17. If the density of the upper brine is assumed to be equal to 1.29–1.37 g/cm<sup>3</sup> (halite–carnallite stage), the density convection gradient would increase to 0.21–0.30. With the value  $I_p$  equal to 0.1, the vertical filtration coefficient ( $K_v$ ) in low-fractured carbonate rocks equal to 10<sup>-4</sup> m/day, and their porosity  $n_0$  equal to 0.05; the descending convection rate of brines from the halogenous basins will not exceed 10 cm/yr (present-day rates of convective brine submergence from the surficial sewer storages into underlying rocks are equal to  $n - n \times 10$  m/yr). There-

fore, at  $V_p = 5$  cm/yr, subsalt rocks with a thickness of 2000 m will be filled with brines during 40 ka. This value agrees with the period of salt-bearing strata accumulation (time of existence of evaporitic basins), which is estimated at  $n \times 10 - n \times 10^2$  ka (Valyashko, 1962).

The brines, enriched in Mg, Br, K, B, and other elements, migrated by free convection from the Lower Permian basins into the underlying Paleozoic complexes before the formation of salt-bearing rocks. Subsequently, the salt accumulation was followed by its compaction, decrease in porosity (from 40–50 to 5% and less) and, as a result, removal of intercrystal Cl–Mg–brine, which also submerged into deep-seated parts of the sedimentary basin. According to (Polivanova, 1982; Sonnenfeld, 1988), the intercrystal brine is squeezed into subsalt complexes when the thickness of salt sequence reaches 200–300 m. In the course of further halogenesis, the hydrodynamic relation between the upper and lower parts of strata, as well as halogenous basin is interrupted. The process of the convective mass exchange gradually slows down and finally stops. Since the Lower Permian, more than 300-m-thick salt sequence was accumulated only in the Bel'sk and Solikamsk depressions of the Volga–Urals Basin, it should be assumed that the relation of the halogenous basin with subsalt complexes existed in its greater part during the whole Late Permian epoch.

It should be presumed that the submergence of brines from the Permian halogenous basin and the primary brine, which was squeezed out of halogenous rocks, as well as their penetrative migration through more aquiclude rocks of the Carboniferous and Devonian occurred not only in hydrogeologic windows of tectonic and lithofacies origin but at the regional scale as well. When estimating their scales, one should bear in mind that the thickness of clays in the mentioned stratigraphical subdivisions is small, and that the permeability of clays relative to brines is considerably higher (up to 10 times and more) than that of fresh water. At the same time, the filtration properties of clay rocks are improved as temperature rises in deeper zones.

For elucidating the formation of subsalt brine reserves, it is of interest to determine the quantity of the primary brine of the Late Permian basin. According to an estimation based on experimental data (Valyashko, 1962), the volume of liquid phase exceeds the volume of segregated salts by factors ranging from 1.9 (halite stage of halogenesis) to 185 (gypsum stage). Approximate calculations had shown that, in the Kungurian Age, when the halogenesis was most extensive, the total volume of the primary brine from the evaporitic basin was measured by millions of cubic kilometers (Zharkov *et al.*). Even the small part of this quantity of brines ( $n \times 10^4$  km<sup>3</sup>) is quite sufficient for filling pores and fractures in Paleozoic and Proterozoic reservoirs.

The density convection is a hydrogeodynamically and hydrogeochemically complicated natural process

including the vertical submergence of brines from halogenous basins, their permeation through clayey (carbonate-clayey) layers, their lateral flow along the local and regional aquicludes (including the basin basement). All of these phenomena are the essence of a mechanism of geological structure filling with epigenetic brines. Simultaneously, less mineralized waters are displaced from subsalt rocks by ascending flows. Eventually, the fate of these waters was related with the surficial evaporitic basin, where they participated in further halogenesis. It is not inconceivable that some water could be accumulated in subsalt rocks of the basin bottom, entering into a geochemical reaction with salts, and promoting the formation of concentrated sodium chloride brines.

As was mentioned, the density convection is realized in a rather narrow interval of geological time and is completed on the disappearance of the positive solution density gradient. Eventually, the Late Permian liquid phase occupied a stable position in subsalt rocks of the Volga-Urals Basin, which marked the completion of the main (sedimentation) stage of the vertical hydrogeochemical zonation.

In the Late Permian epoch, the scales of halogenesis were sharply reduced: in the Ufimian Age, evaporitic basins existed in the Solikamsk Depression and adjacent regions; in the Kazanian Age, they existed in the Buzuluk Depression. However, the density convection did not gain any significant development, because the Carboniferous and older complexes were shielded by thick strata of the Kungurian salts.

The Mesozoic and Cenozoic eras present a subaerial stage of basin evolution, when, on one hand, the infiltration waters penetrated into the upper part of the subsalt rocks and mixed with sedimentogenic-epigenetic brines, and, on the other hand, the mineralization and ion-salt composition of brines were balanced, as a result of convective-diffusion and diffusion processes. The dehydration transformation of gypsum into anhydrite also had a diluting impact upon the brines. But it should be assumed that if the sedimentation brines were somewhat freshened, this could be only in the upper part of the subsalt strata. It is hardly probable that in the middle and lower parts of the basin, which were filled with heavy brines, low-mineralized waters could penetrate in perceptible quantities. Moreover, in regions with the complicated structure of the halogenous Kungurian strata (gypsum, salt), the dehydration solutions could migrate through salts and be saturated with readily soluble sodium chlorides. Therefore, it is no use discussing any freshening of sedimentogenic brines in this situation.

The submergence of Na-Mg chloride brines, i.e., the liquid phase (LP) of a halogenous basin, was accompanied by their metamorphization as a result of interaction with rocks, as well as rock composition alteration owing to dolomitization, albitization, exchange adsorption, and other processes:

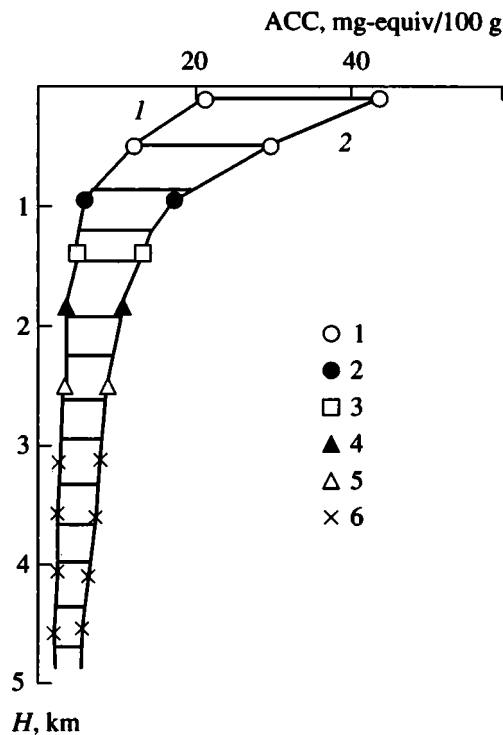
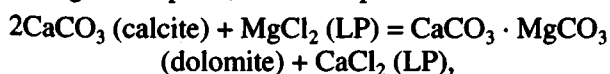
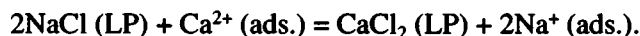
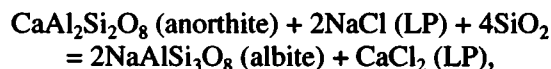


Fig. 2. Variation in the absorbed complex capacity (ACC) of sandstones (curve 1) and mudstones (curve 2) vs. depth. Rocks: (1) Permian, (2) Middle Carboniferous, (3) Lower Carboniferous, (4) Devonian, (5) Silurian, (6) Lower Proterozoic.



Experimental studies of the exchange-adsorption properties of the Paleozoic and Proterozoic terrigenous rocks (Popov, 1990) have shown that the emergence of sediments in the upper part of the hypergene zone and in the catagenesis zone (depth >1000–1500 m) is accompanied by their compaction and lithification, and the capacity of the absorbed complex is regularly decreased (Fig. 2). The capacity amounts to 70–100 mg-equiv/100 g for Permian sediments; less than 20–25 mg-equiv/100 g for Middle Carboniferous sediments; less than 10–15 mg-equiv/100 g for the Lower Carboniferous; and less than 5–10 mg-equiv/100 g for the Devonian, Silurian and Upper Proterozoic. The capacity of mudstones is always higher than that of sandstones. The differences in their adsorption properties are particularly great in the hypergene zone; in the catagenesis zone, they are less essential. The low capacity of rocks is caused by both simplification of the structure of the montmorillonite-chlorite-series clay minerals and the physicochemical peculiarities of the catagenesis zone. In this case, the *PT* parameters and, apparently, geological time, which influence the aging

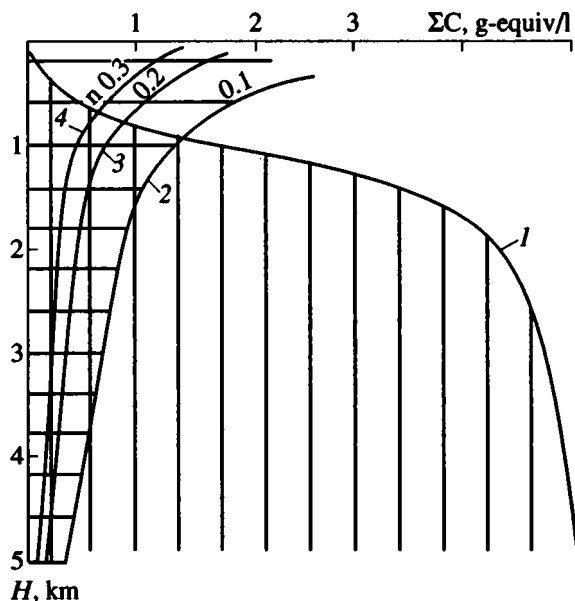


Fig. 3. Variation in concentrations of hydrated cations (curve 1) and adsorbed cations, which can enter groundwaters with various porosity (curves 2, 3, 4), vs. depth.

of colloids and their transition from the exchange state into the nonexchange one, are of great importance.

Usually, Ca and Mg dominate in the exchange complex of the Paleozoic mudstones (being, apparently, syngenetic with this rocks). Sandstones have a more variegated composition of the exchange bases (Ca-Na, Mg, K-Na, and others), which is governed by the geochemistry of the sedimentogenesis and subsequent processes of the cation exchange with brines. The absorbed complex of the Proterozoic formations lying at the depth of 1600–4700 m in conditions of the late catagenesis and metagenesis is specific. No exchange Mg is contained in mudstones and shales, but K is abundant (up to 64%). Calcium and magnesium are predominant in the absorbed complex of sandstones.

It is important to emphasize that a certain relation between cations of the absorbed complex of rocks and contacting brines is absent. The bases adsorbed by clayey rocks are compositionally much more diversified than major cations of brines. No distinctive dependence of the degree of their metamorphization on the absorbed K concentration and the total exchange capacity is observed. There is no analogs for the Mg type of the absorbed complex among subsalt brines. At the same time, it is obvious that, with the depth, the hydrogeochemical role of ion exchange inevitably decreases, since not only the tenfold drop of the rock adsorption activity occurs, but the simultaneous increase (10–20 times) in the water mineralization takes place. In these conditions, no more than 200–500 mg-equiv/l cations can pass from the absorbed complex into brines. This value is incomparably less than the concentration in hydrated state (3000–

5000 mg-equiv/l (Fig. 3). Therefore, adsorbed hydrated ions can account for 5–10% at the depth of up to 2000 m, whereas the proportion of exchange cations in brines will not be over 1–3% at the depth of 3000–5000 m.

In this respect, the following example is demonstrative. Let us assume that sodium chloride with a mineralization of 250 g/l would flow into rock with a porosity of 0.2 and 5 mg-equiv/100 g of exchange Ca. After the complete substitution of Ca in absorbed complex for Na, the brine will contain about 5% Ca, which will cause the decrease in coefficient  $r_{Na/rCl}$  from 1.0 to 0.96. Hence, the metamorphizing effect of the exchange reaction is small under given conditions typical for the Paleozoic basins. Inasmuch as the reserves of absorbed Ca will be exhausted due to cationic exchange and deep-seated generation sources of new colloids are practically absent, the rock metamorphization (consequently,  $CaCl_2$  content) will decrease during the repeated percolation of infiltrational brines in these rocks.

It follows that ion-exchange reactions in terrigenous rocks cannot exert an essential metamorphizing effect on the composition of deep-seated brine waters, especially as we take into account the negligible distribution of these rocks in the Paleozoic and the low capacity of the cavernous and fractured carbonate rocks, which, as is mentioned, comprise up to 90% of the Paleozoic sequence.

The hydrolytic interaction between the buried primary brine and terrigenous aluminosilicate rocks (albitization of feldspars, analcimization of zeolites, and others) can exert a great effect on its composition. The study of the composition of Paleozoic and Precambrian aluminosilicates in the Volga-Urals Basin has shown that they were subjected to certain postsedimentary transformations under the action of brines and, first of all, decomposition of endogenic aluminosilicates with the formation of several authigenic minerals (albite, kaolinite and others). However, because of the limited development of terrigenous rocks in the lower stage of the basin, it is beyond reason to attach a leading significance to these processes in the formation of chlorocalcium brines.

The lithohydrogeochemical environment of the region was such that the formation of Na-Ca chloride brines was mainly governed by the metasomatic dolomitization of limestones, rather than the adsorption and hydrolytic processes in terrigenous rocks. The dolomitization proceeded under the influence of Cl-Mg brines penetrating from the Permian evaporitic basins through limestones. Because of their exclusive enrichment in Mg, the brines have a very high capability for dolomitization.

Prolonged metasomatic processes caused cardinal changes in subsalt carbonate rocks of the Volga-Urals Basin and the formation of secondary (dia- and epigenetic) dolomites, which are widespread in the Lower

Permian, Carboniferous, Devonian, and Riphean sediments. The secondary features are observed as the metasomatic replacement of calcite by dolomite, inconsistency of dolomitization, its selective character, and others. The total thickness of secondary dolomitized rocks ranges from a few meters to 140 m in individual stratigraphic subdivisions and amounts to several hundreds of meters in the Riphean. Within various parts of the basin, their total thickness ranges from 160 to 400 m, which comprises 20–30% of the thickness of the Paleozoic strata. The Mg content in rocks amounts to 10% (13.2% in chemogenic dolomite).

The lithofacies analysis and the lithogeochemical appraisal of carbonate rocks have shown an agreement between Ca in brines and Mg in secondary dolomites (Popov, 1989). Therefore, the quantity of Ca, released from limestones during metasomatic processes, is quite sufficient for the formation of Cl–Ca brines of appropriate geochemical character in the sedimentary cover of the basin. It is remarkable that, at the present, the most metamorphosed Na–Ca brines of the Volga–Urals Basin have very low  $rMg/rCa$  value (0.05–0.2). These data and results of the thermodynamic analysis of the dolomitizing capability of brines of various geochemical types testify to the replacement of Ca from limestones by Mg of brines.

It should be emphasized that the epigenetic dolomitization resulted in an essential increase in porosity (by 10–12%) and permeability (tens times) of carbonate rocks, i.e., formation of secondary reservoirs of oil, gas, and industrial mineral waters.

The natural consequence of the halogenesis, density convection, and later processes of interaction in the primary brine–rock system is the selective accumulation of microelements in various geochemical (genetic) types of brines. As is mentioned, the maximal concentrations of Br, B, K, and rare alkaline elements are confined to inter- and intrasalt Mg chloride brines. All of these elements, except for B, are also accumulated in deep-seated (>1.5 km) sedimentogenic–epigenetic Na–Ca chloride brines. The fate of B was different. In the processes of metasomatic dolomitization, B coprecipitated with Ca, which migrated from carbonate rocks in the form of low-soluble calcium borates. Therefore, soda infiltrational sodium chloride brines are more enriched in B.

Iodine is more indifferent to the physicochemical properties of water medium; it does not form accumulations in liquid or solid phases of halogenesis and is contained in them in extremely small quantities. Relatively low-metamorphosed ( $rNa/rCl = 0.7–0.9$ ) Ca–Na brines, often having poor mineralization (60–100 g/l) and included into the Paleozoic organic-rich limestones of the Cis-Urals Foredeep at the depth of 0.9–2.2 km, are mostly enriched in B. The stressed tectonic situation, evolved in the conjugation zone between the Russian Platform and the Urals during the Hercynian folding, favored the rise of paleotemperatures in the fore-

deep and, as a consequence, the migration of I from rocks.

The crucial role of the Permian halogenesis and density convection in formation of brines is supported by results of their absolute age determination by He–Ar and kineticogeochemical methods (Popov, 1994). The latter is based on the study of the replacement of Ca from the host rocks by Mg of the liquid phase. In most cases, Middle and Early Paleozoic sediments contain Early Permian (200–250 Ma) brines; i.e., they are sedimentogenic–epigenetic.

## CONCLUSIONS

From the aforementioned, it follows that the gravity is the main regulator of the subsalt brine zone in sedimentary basins with halogenous formations. It is planetary gravity forces that caused the differentiation of groundwaters by density, the migration of most concentrated brines from the surficial evaporitic paleobasins in underlying rocks, and their localization in most subsided parts of structures. Processes of epicontinental salt accumulation, density (concentration) convection, and metamorphization of halogenous brines at the stages of diagenesis and epigenesis exerted exclusively great influence on the lithogeochemical state of the underground hydrosphere. In the Volga–Urals Basin, composed of predominantly carbonate rocks, these processes were responsible for the formation of the enormous mass of polycomponent chlorocalcium-type brines, the metasomatic dolomitization of the Paleozoic and Proterozoic limestones, and the growth of their capacity and filtration parameters.

## ACKNOWLEDGMENTS

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# Paleogeography and Facies of the Central and Northeastern Parts of the Moscow Syncline in the Devonian

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**Abstract**—New data on the stratigraphy and composition of the Devonian rocks of the Moscow Syncline were used. Facies–paleogeographic schemes were compiled for the Lochkovian, Eifelian, Givetian, early–middle Frasnian, late Frasnian, and early–late Famennian evolutionary stages of the Moscow Syncline. Seven sedimentation cycles were developed due to sealevel fluctuations and structural rearrangements in the paleoceanic basins surrounding the East European Platform at that time. The inference was made on the structural heterogeneity of the platform basement and on differentiated movements as well as on the strike-slip fault nature of some fragments of the basement relative to each other in the Devonian.

A series of works on the stratigraphy, paleogeography, and tectonics of the East European Platform was published recently (*Tektonika...*, 1991; *Mezhdunarodnaya...*, 1998; Rodionova *et al.*, 1995; Tikhomirov, 1995; Nikishin *et al.*, 1996, and others), which summarized, to a great extent, the results of long-standing studies. However, all those generalizations, undeniably valuable, leaned upon data on stratigraphy and geophysical evidence obtained from boreholes. Observations on the internal structure, sedimentational structures of rocks, and particular depositional environments remained unused. Besides, until recently, the Devonian rocks of the northeastern Moscow Syncline were least studied because of a poor core material available for some intervals of the section, especially for the Givetian and Famennian.

The use of new data on the stratigraphy and composition of the Devonian rocks in the Moscow Syncline, the spatial distribution of basic section types, the basement structure (Fig. 1), as well as acquisition and retrieval of literature information on lithologic specific properties of rocks, make it possible to assess paleogeographic environments more adequately, to distinguish particular structures, to trace the results of structural rearrangements in the Moscow Syncline, the time of appearance and the life-time of individual structures, as well as the temporal displacement of structural–facies zones and in some cases to reveal the causes of structural reconstructions.

The Devonian rocks are widely developed on the territory discussed and occur at a depth from 500 to 2400 m, the total thickness being 1000 m. The composition of rocks and the completeness of stratigraphic sections at different areas vary widely. Five types of sections and related structural–facies zones confined to

different parts of the recent platform structure are distinguished (Fig. 1): (I) the Fennoscandinavian megablock; (II) the Central Russian Aulacogen; (III–V) the Volga–Urals megablock: (III) the Galich Depression; (IV) the southern slope of the Moscow Syncline, and (V) the Kotel'nich Arch. Terrigenous rocks dominate in the type I section, whereas carbonate rocks prevail in the type IV section. Sections of types II and III are noted for a diverse rock composition. The type V section lacks Lower and Middle Devonian rocks.

## THE EARLY DEVONIAN

### *The Lochkovian (Pirogovo) Time*

The Lochkovian time interval is characterized by the Pirogovo Formation (Birina, 1957; Rodionova *et al.*, 1995), which represents a complex of variegated, mainly terrigenous rocks. The carbonate material is present in the form of cement only. The rocks transgressively overlap the Vendian and Silurian rocks and are overlain with erosional unconformity by the Emsian (Lower Devonian) rocks. The thickness of the Pirogovo Formation rocks varies from 10 to 180 m and depends mainly on the extent of the subsequent erosion.

The Lochkovian rocks are divided into three (sandstone, siltstone–mudstone, and siltstone–marls) facies (Fig. 2).

The **sandstone facies** is developed in the northeastern part of the recent domain of the Pirogovo Formation. The facies represents a member of variegated sandstones comprising separate interlayers of dark brown, dark greenish gray siltstone, mudstone, and mudstone-like and silty clay. The thickness of the rocks often exceeds 100 m. Sandstones are fine- and medium-grained, often coarse-grained and variegated (the

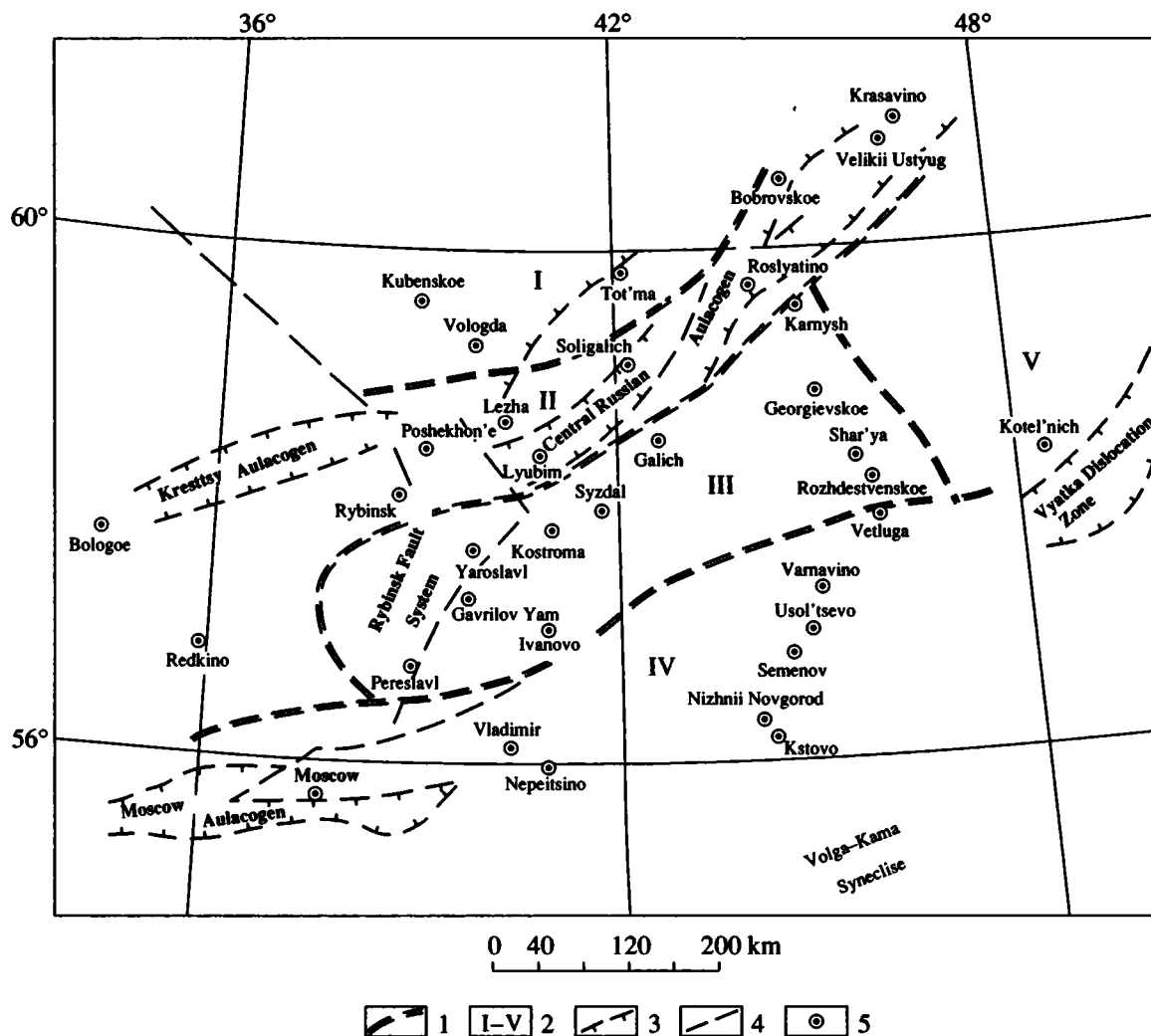


Fig. 1. Scheme of faults in the basement of the central East European Platform (*Mezhdunarodnaya...*, 1981, 1998). (1) Boundaries between different types of geological sections and structural-facies zones; (2) number of basic section types; (3) faults bounding the Riphean aulacogens; (4) other faults; (5) boreholes.

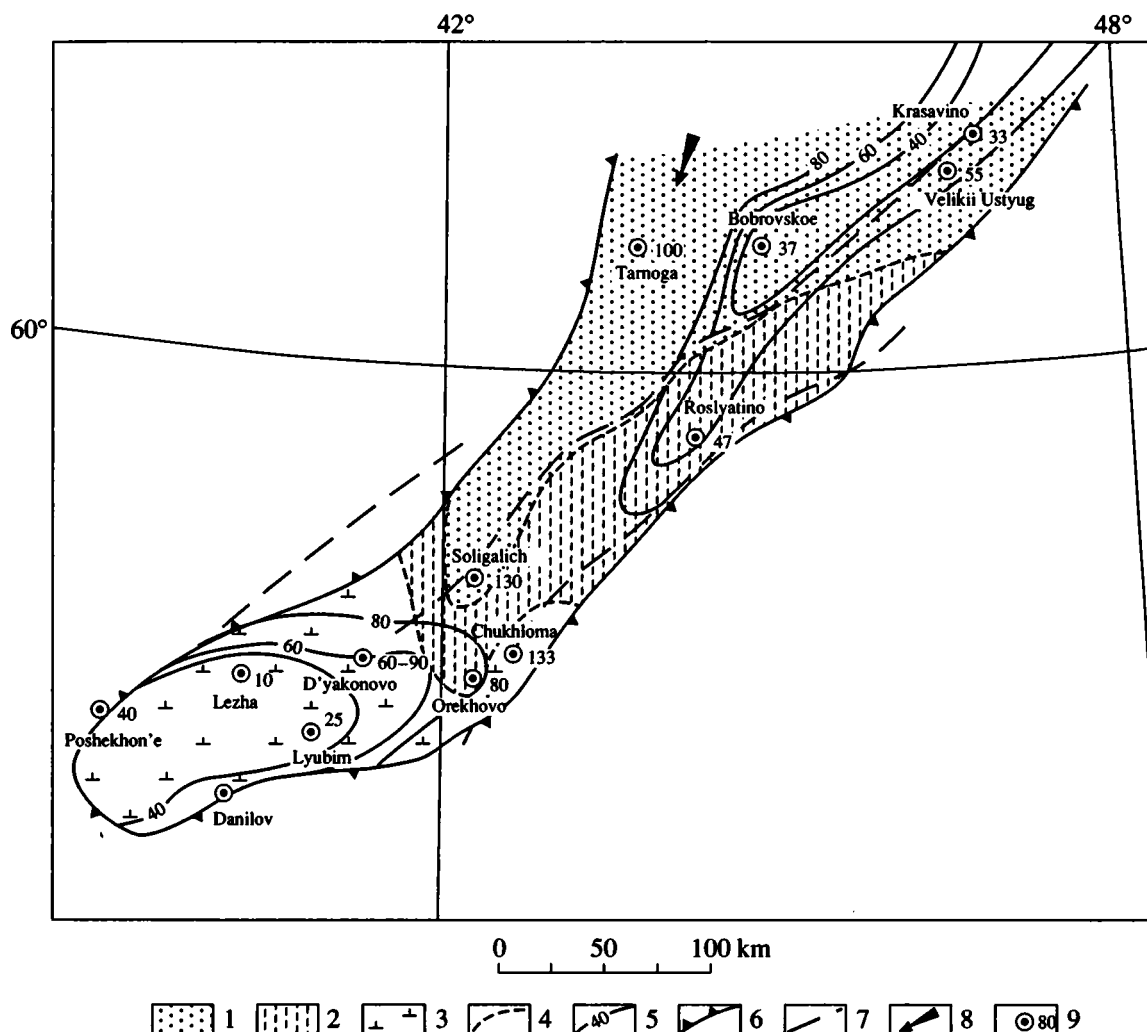
grain size varies from 0.06 to 0.9 mm). The color varies from light gray, gray, and greenish gray to red-brown and light brown. Sandstones are composed of quartz, quartz-feldspar, or feldspar-quartz (plagioclase-K-feldspar) aggregates. In coarse-grained and variegated varieties, Birina (1957) has described layers of rounded gravel- to pebble-size fragments of red-brown clay, as well as small pebbles of cherts. Garnet and tourmaline dominate among accessory minerals. Zircon and ore minerals are less abundant. A considerable admixture (up to 50%) of weathered grains has been found in the Soligalich Borehole. Cement in sandstones is abundant and argillaceous. Secondary carbonate cement is encountered in places. The clastic products are rounded and angular-rounded.

Uniform, thin-laminated, wavy- and oblique-laminated structures are characteristic of the sandstone facies. Structural features, the abundant argillaceous

admixture, along with poor grading and roundness of clastic products of the facies, indicate the intense influx and quick burial of the clastic material. It seems that conditions for repeated rewashing and redeposition of the clastic material were rare during the accumulation of rocks, indicating fast subsidence of the basin bottom. A submarine clastic fan or probably submarine delta may be assumed to exist.

The **siltstone and mudstone facies** was penetrated by the Roslyatino and Orekhovo boreholes. The facies is characterized by thin alternation of mudstone, mudstone-like clay, and siltstone. The rocks are dark brown, reddish brown, in places spotty. Siltstones are often greenish gray. Clay varieties of rocks comprise an admixture and thin laminae of clastic quartz of a silt and sand size. Rocks have a very thin horizontal bedding. The considered facies is likely to characterize a more distal part of a submarine delta or a fan made up of the





**Fig. 2.** The facies–paleogeographic scheme for the Lochkovian. (1) Proximal zone of the submarine delta; (2) distal zone of the submarine delta (silt–clay facies); (3) littoral zone (carbonate–clay facies); (4) facies boundaries; (5) isopachs; (6) present-day boundary of Lochkovian sediments; (7) active faults; (8) direction of clastic material influx; (9) boreholes and thickness of sediments.

sandstone facies in the proximal part. A decrease in the grain size of rocks from north to south indicates that the bulk of the clastic material was derived from the north (in current coordinates), i.e., from the Pechora Basin where, according to recent data (Nikishin *et al.*, 1996), uplifting and intense dislocations related to the final stages of the Caledonian orogeny got under way at that time. It is possible that remains of the pre-Riphean weathering crust were subjected to washout, as evidenced by the presence of weathered grains in sandstones. An intense supply of the clastic material by fresh water from land probably caused a certain freshening of the basin in the Pirogovo time. Therefore, the Pirogovo Formation rocks are depleted in organic fossils.

The **mudstone and marl facies** is developed in the southwestern area of the present-day Pirogovo Formation domain. It was penetrated by the Chukhloma, D'yakonovo, Lyubim, and Danilov boreholes. The

D'yakonovo Borehole yielded the most complete section. Two sedimentation cycles 50 m thick are distinguished there. Fine-grained sandstone and siltstone dominate at the base of each cycle, whereas reddish mudstone, clay, as well as calcareous siltstone with thin dolomite interlayers, prevails at the top of the cycles. In composition and texture, terrigenous rocks are similar to rocks of the siltstone and mudstone facies. Dolomites are light or dark gray (greenish gray in some interlayers) and rich in clay material. The cyclic nature of the facies structure reflects fluctuations in the history of the Early Devonian transgression or recurrent intensification of the clastic material influx due to nonuniform growth of the Caledonian orogens in the provenance.

Carbonate rocks of the Pirogovo Formation are likely to assume a greater significance in the southwesternmost part of the region (the Poshekho'e Borehole). Organic fossils are more common there. The mudstone

and marl facies characterizes a relatively deep area of the littoral zone in the Pirogovo Basin, which is far from the provenance, and represents a relic structure. The presence of the facies in the extreme southwest indicates that the Pirogovo Basin was spacious and extended at least over the central part of the Moscow Syncline. The preservation of rocks of this facies only within the graben of the Central Russian Aulacogen is explained by the dominating submergence of the structure during the ensuing epoch.

The internal structure of the Pirogovo Basin cannot be judged by changes in the thickness of the Pirogovo Formation rocks, even as abrupt changes in the thickness do not result in facies changes (Fig. 2). In particular, the thickness of sections in the Tarnoga, Bobrovsk, Lezha, and D'yakonovo boreholes accounts for the extent of their preservation in the recent structure. Data available are inadequate to reveal small synsedimentary structures. The former existence of rather a large clinoform (probably a prodelta), the fragment of which survived in the northeastern part of the Pirogovo field is open to discussion. It is likely that movements took place along the Soligalich Fault in the Pirogovo time, its northern flank plunging more intensely as the thickest sandy facies are developed in the northern wall.

The recent structure of the Pirogovo Formation rocks does not coincide with the paleostructure of the Pirogovo Basin and reflect only a later inversion of the Central Russian Aulacogen and the growth of a horst between the Soligalich and Chukhloma faults, most likely, in the Carboniferous. The inversion seems to be responsible for the present-day thickness of the Pirogovo Formation.

The sedimentation phase of the earlier half of the Lochkovian was followed by a remarkable hiatus lasting over a later half of the Lochkovian, Pragian, and an earlier half of the Emsian. The hiatus is related to the final stages of the Caledonian orogeny. A new extensive sea transgression to the territory of the Moscow Syncline, as well as a new sedimentation cycle started only in the latest Early Devonian (late Emsian).

#### *The Emsian (Ryazhsk) Time*

An accumulation of the Ryazhsk Formation (Filipova, 1962), corresponding in age to the Ryazhsk Horizon of the upper Emsian, proceeded at that time. The Ryazhsk Formation is penetrated by many boreholes and represented mainly by fine-grained sand and sandstone consisting of sand and feldspar-quartz aggregates and argillaceous or dolomite cement. According to Tikhomirov's data (1995), coarse-grained sand and gravelstone occur at the base. Sandy deposits also comprise rare interlayers of clay and siltstone. For instance, at the stratigraphic datum (Pärnu Bed), in the Lyubim Borehole section, Birina (1957) described light gray and white, mainly quartzose sands with small pyrite concretions comprising laminae of greenish gray clay

with detritus of carbonified plant remains. Their thickness makes up 14 m. In the upper part of the member, sandstones give way to microlaminated silty clays, 7 m thick, with plant remains. Sands are mainly fine-grained, coarse- and medium-grained in some interlayers, obliquely laminated, weakly cemented with carbonate or clayey cement. Zircon sharply dominates in the heavy fraction. Besides, glauconite is present as well.

Facies changes at the territory discussed are poorly expressed. Only changes in the thickness from 0 to 40 m are observed. Moreover, the amount of clay and siltstone interlayers in the upper part varies from section to section. Organic remains are rare and poorly preserved in the Ryazhsk Formation rocks. In general, it is a typical coastal-marine association of a transgressing basin.

Rocks of the Ryazhsk Formation unconformably overlie the basement rocks, the Vendian Povarovka Formation, as well as the Ordovician, and Silurian (Lochkovian) Pirogovo Formation rocks, marking the onset of a new cycle of a major sea transgression onto the territory of the Moscow Syncline. The transgression was maximal in the Eifelian. The present-day Ryazhsk Formation domain, which is wider than that of the Pirogovo Formation, is delineated by the washout surface formed during the structural rearrangement of the platform at the beginning of the Givetian.

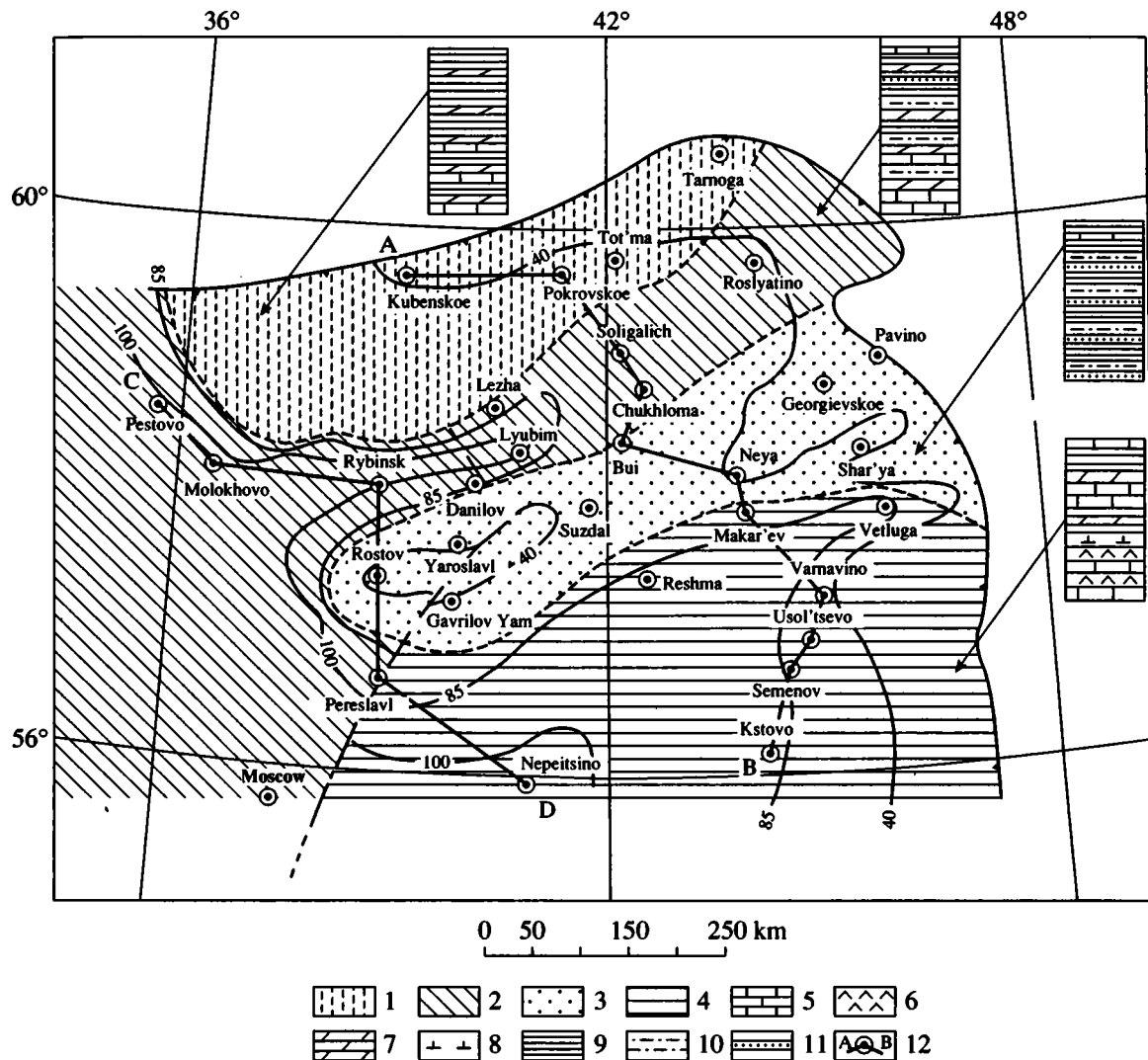
According to Tikhomirov's data, the clastic material was derived from the south (the Voronezh Massif) and the north in the Ryazhsk time. The intensity of the influx of clastic products and their coarseness decreased with time. It suggests a widening of the basin in the Ryazhsk time. The saline regime of the basin in the Ryazhsk time was unstable and differed from normal conditions due to freshwater inflow from land. The basin was mainly populated by fish and lingulids. Tikhomirov reckons that the Ryazhsk Basin of the Moscow Syncline was freely connected with the basin of the Baltic Syncline.

### THE MIDDLE DEVONIAN

#### *The Eifelian Age*

The terrigenous-carbonate association rocks of complicated composition, 30–100 m thick, accumulated and altered throughout the Eifelian (Figs. 3, 4). They occur on the upper Emsian rocks without a hiatus. Eifelian rocks are missing within the Kotel' nich Arch.

Sulfatized and dolomitized limestones with marl and clay interlayers at the base and roof accumulated within the region discussed in the early Eifelian (Dorogobuzh–Klintsy) time. Throughout the Eifelian, rocks are mainly represented by sandy-clayey fractions only in the type III sections in the area between the Central Russian and Moscow Aulacogens. The thickness of the rocks varies from 30 to 60 m.



**Fig. 3.** The facies-paleogeographic scheme for the Eifelian. (1) Lagoon slope (clay-carbonate facies); (2) lagoon zone with stagnant sedimentation (clay-carbonate facies); (3) submarine delta zone (sand-clay facies); (4) bay-lagoon zone with a high water salinity (anhydrite-limestone facies); (5) limestone and dolomitized limestone; (6) anhydrite; (7) clayey limestone and marl; (8) carbonate clay; (9) clay; (10) siltstone; (11) sand and sandstone; (12) see Fig. 4 for profiles and Fig. 2 for other symbols.

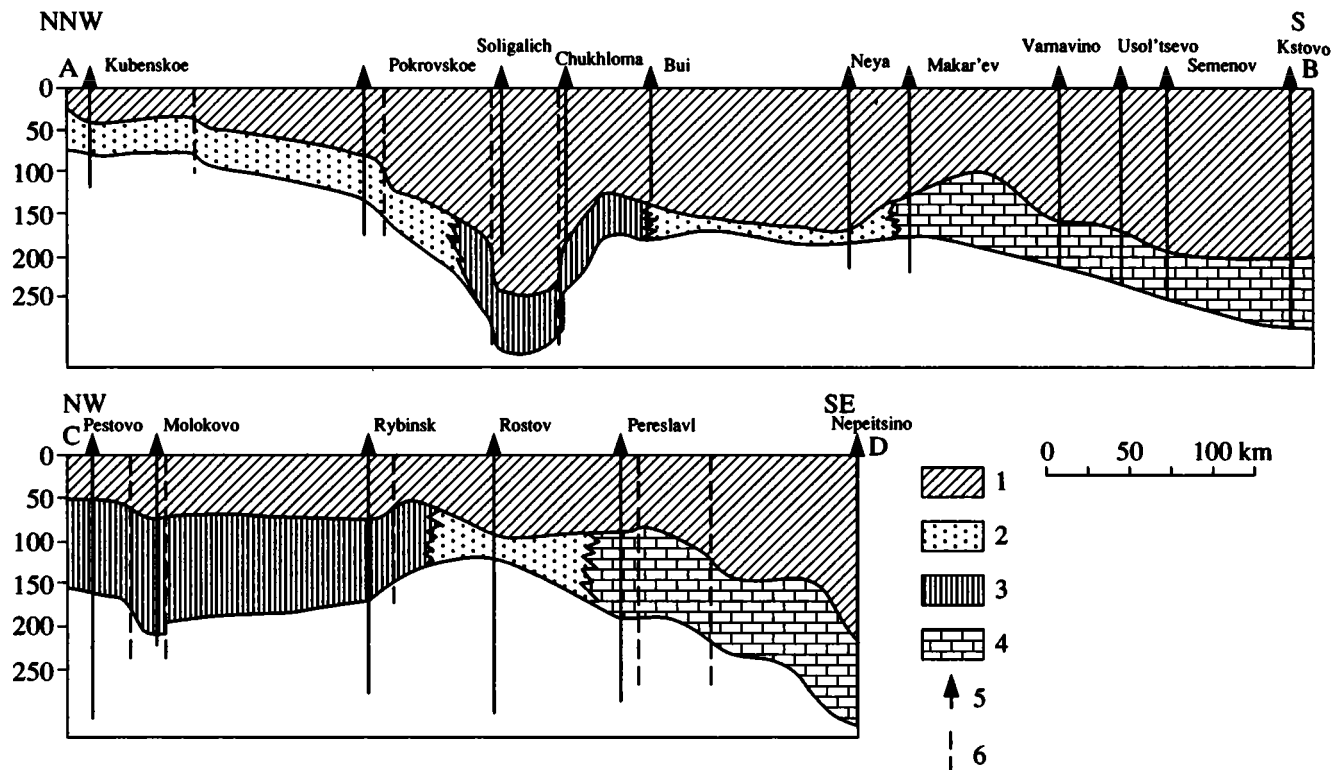
Anhydrite-carbonate rocks give way to carbonate-clayey rocks in the southern part of the region in the middle Eifelian (Mosolovo) time. Limestones, gray, brown-gray or greenish gray in color due to some clay admixture, dominate in the lower part. Limestones become clayey upward the section, comprising numerous thin interlayers of greenish gray clay and imprints of poorly preserved fauna. Further upward, dark gray mudstone-like clays with pyrite impregnation and patches dominate. The clays comprise some silt admixture and several clayey limestone interlayers, 0.2–0.4 m thick. The Mosolovo rocks are crowned by dark gray and yellowish gray clastic limestone.

Clayey rocks become dominant in the northern part of the region where sections of types I and II are common. Calcareous clay and marl with separate interlay-

ers of clayey limestone prevail in the lower half of the Mosolovo Bed. The upper half comprises calcareous clay with siltstone interlayers.

In the latest Eifelian (Chernoyarsk) time, rocks corresponding in age to the Chernoyarsk Horizon differ from underlying Eifelian rocks in a lower carbonate content and greater admixture of the clastic terrigenous material. The rocks are mainly represented by dark gray clay and siltstone, in places with limestone interlayers. Siltstone and sandstone dominate in some sections. The thickness of the rocks varies from 10 to 20 m.

Rocks of the Chernoyarsk Horizon terminate the Emsian-Eifelian sedimentation cycle. They are unconformably overlain by Givetian sediments. Due to wash-out in the earliest Givetian, the Chernoyarsk rocks survived only in fragments. More complete sections are



**Fig. 4.** Structural-facies sections for the Eifelian-Givetian. (1) Givetian Stage, coastal-marine terrigenous rocks; Eifelian Stage: (2) coastal-marine terrigenous rocks, (3) clayey-carbonate rocks in a stagnant basin, (4) sulfate-carbonate rocks in a basin with a high water salinity; (5) boreholes; (6) faults.

revealed in the southern part of the territory where the offshore facies are noted for a higher carbonate content. Relatively complete sections are found at the territory of the Central Russian Aulacogen, although, carbonate material is missing there and sandstone appears at the base of sections.

Rocks of the Chernoyarsk Horizon complete the sedimentation cycle which began in the latest Emsian with a sea transgression onto the Moscow Syncline following a major structural rearrangement. The peak of the transgression falls within most of the Eifelian. The sealevel drop at the end of the Eifelian, at the territory under consideration is confirmed by the regressive nature of sediments in the upper parts of the Mosolovo and Chernoyarsk horizons. Facies conditions became more uniform at that time, and clay sedimentation became dominant at the whole territory.

The data on the composition of the Eifelian rocks allow us to make conclusions on the facies, the paleogeography, and paleostructure of the sea basin located in the northeastern part of the Moscow Syncline at that time.

The obtained results are shown in Fig. 3. Four (anhydrite-limestone, clayey-carbonate, limestone-dolomite, and sandy-clayey) facies are distinguished, which characterize sedimentation features and paleo-

geographic conditions in the Moscow Syncline during the Eifelian.

The **anhydrite-limestone facies** makes up sections in the southernmost part of the territory. It consists of dark gray and yellowish gray, thinly and obliquely laminated, organogenic-clastic, carbonate-clastic and silty limestones with the terrigenous admixture and anhydrite interlayers. The facies characterizes distal (relative to clastic material source) areas of the shallow-sea basin with an unstable salt regime. The anhydrite-limestone facies zone was characterized by active hydrodynamic regime, water currents, regular turbidity, along with disintegration, redeposition, and probably a partial dissolution of unconsolidated sediments. Numerous traces of the layer-by-layer washout suggest the presence of storm-related sediments (tempestites). It is not improbable, though, that traces of dissolution of gypsum or anhydrite interlayers could be mistaken for the washout surface in drillcore descriptions. The thickness of the anhydrite-limestone facies rocks is approximately 30 m.

The **clay-carbonate facies** is developed in the northern area of the first structural-facies zone. The facies occupied a vast area in the later half of the Eifelian. It is mainly composed of calcareous clay and marl. The amount of dark gray calcareous clay gradually increases and siltstone appears in the upper part. The

facies characterizes the basin zones with a calm hydrodynamic regime and a combined accumulation of fine clayey and silty carbonate material. Stagnation and a slightly higher water salinity could result in diagenetic dolomitization of limestones. Clayey products are likely to be derived from the Baltic Shield, though part of them arrived from the Kotel'nich Uplift, especially into the Central Russian Aulacogen (type II section) and the southern parts of the region (type IV section).

The **limestone-dolomite facies** is closely associated with the clayey-carbonate facies along the lateral and vertical profiles in the Central Russian Aulacogen. In depositional environments, the facies is similar to the adjacent clay-carbonate facies. However, the limestone-dolomite facies is characterized by a more intense carbonate accumulation, as well as an influx of clastic products of the clay, silt, and even sand (e.g., fractions the Lyubim Borehole). Moreover, a higher salinity caused intense dolomitization and sometimes anhydrite formation. The thickness of rocks varies from 25 to 65 m. It may be suggested that the clay-carbonate and limestone-dolomite facies characterize a bay or lagoon populated by abundant but uniform fauna. The lagoon was probably separated from the sea basin with a changing salinity, the northeastern part of which was located in the southern part of the region. The third structural-facies zone played the role of a barrier. An uplift located in the zone served as a provenance for the clastic products. It is confirmed by the fact that more abundant and coarse-grained material was found in the second structural-facies zone and in the northern part of the fourth zone in the lowest Eifelian section. Mainly terrigenous sediments accumulated there since the Klinttsy time and the Kotel'nich Arch served as a source area for them.

The **sand-clay facies** is typical of the third structural-facies zone. It extended southward and northward only in the later half and especially at the end of the Eifelian. The facies is made up of variegated mudstones with interlayers of siltstone and, in places, sandstone and limestone. Carbonized plant remains are sporadically found in it. The violet-brown and greenish gray, compact or clayey mudstones contain different amounts of silty or sandy admixture. Siltstones are violet-brown, gray, greenish gray, irregularly clayey, and include intraclasts in places. The thickness of the rocks depends on the extent of the subsequent washout and varies from 10 to 46 m. Organic remains are few in number and often poorly preserved. Inarticulate brachiopods dominate. The facies characterizes conditions of the intense influx and burial of the terrigenous material. The sedimentation rate often exceeded the subsidence rate. The supercompensation of subsidence by sedimentation was also occasionally registered. Clastic products, which were accumulated as a wide delta fan in the Galich Depression, were partially carried away by currents over the rest of the basin, enriching carbonate sediments of the background sedimentation in clayey and sometimes silty and sandy material. Most of

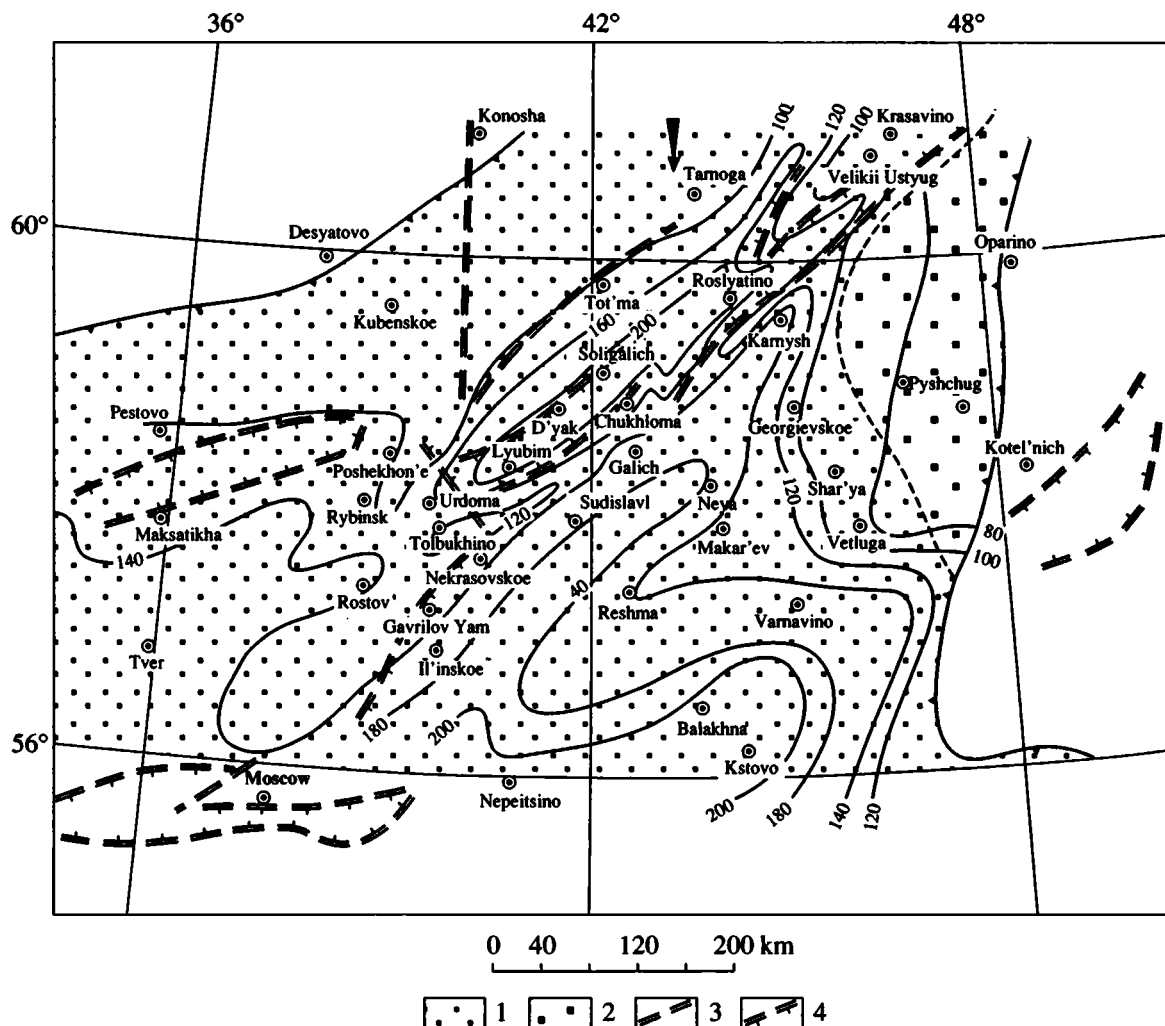
the clayey material was deposited in the southern region (the fourth structural-facies zone) in the earlier half of the Eifelian. Subsequently, most clastic products precipitated in the northern lagoon that was being silted up.

Thus, we may assume the existence of a prodelta, which accumulated clastic products from the Kotel'nich Arch, in the third structural-facies zone in the Eifelian, suggesting a growth of the Kotel'nich Arch at that time. The arch and the deltaic sedimentation area of the third structural-facies zone separated two troughs. The southern trough corresponds to the fourth structural-facies zone characterized by the prevalence of anhydrite-carbonate and carbonate-clayey sedimentations. The trough apparently represented a bay of the main basin of the Eifelian Russian Plate, but was locally separated from the basin by submarine rises.

The northern trough, which existed in the second structural-facies zone above the Central Russian Aulacogen, represented a narrow bay of the main basin as well. Calcareous clay and marl along with dolomitized carbonate sediments accumulated there. In the later half of the Eifelian (the Mosolovo and Chernoyarsk times), the sea basin on the territory discussed became more open as compared to the previous epoch. Because of this, such minerals as dolomite and anhydrite disappeared from sediments. An increase in the amount of terrigenous material at the terminal Eifelian is likely to be related to a new pulse of uplifts in the Kotel'nich Arch area and a general reduction of the basin area. We may also assume a certain uplift (or relatively slow subsidence) of the fourth structural-facies zone during the Mosolovo time. The subsidence lag protected the fourth structural-facies zone, at least at the beginning, against the influx of clastic products that created environments favorable for the limestone accumulation.

### *The Givetian Age*

Givetian rocks occur with erosion on different Eifelian horizons to begin a new, predominantly terrigenous sedimentation cycle. Upward, the Givetian rocks are unconformably overlain by the lower Frasnian rocks. Sands and fine-grained, light gray and greenish gray quartzose-feldspathic sandstones dominate in Givetian rocks. Also present are separate interlayers of coarse-grained bituminous and clayey varieties. The yellowish gray clayey varieties comprise glauconite grains and remains of carbonified plant detritus. The sandstone cement represents a regenerated quartzose or clayey material. The Givetian rocks are similar in lithology on the whole territory discussed. Only the clay content slightly increases toward the south. It is likely that facies changes on the territory are poorly studied because of a low core recovery in the course of drilling. Terrigenous rocks are distinguished for poor sorting of clastic material that indicates a fast accumulation and burial rate. It is noteworthy that abrupt and sometimes contrasting changes in the thickness of the Givetian



**Fig. 5.** The facies–paleogeographic scheme for the Givetian. (1) Submarine delta zone (sand–clay facies); (2) shoals of intrabasin rises (sand facies); (3) faults; (4) normal faults.

rocks are not accompanied by marked changes in the nature of sediments (Figs. 4 and 5). It is only within the Kotel'nich Arch (the fifth structural–facies zone) that thin terrigenous deposits transgressively overlap the crystalline basement or the Vendian rocks. Light, fine-grained, quartzose sandstones with wavy and cross lamination dominate among the terrigenous rocks. Clastic products in sandstones are well sorted and rounded. They represent shallow-water products, which were subjected to repeated washout and redeposition ("skeletal sands") under extreme shallow-water conditions. This is also confirmed by a mixed fauna found in these rocks. Sandstones comprise thin bands of thin-laminated and lenticular mudstone and clayey siltstone with fragments of carbonified plant detritus. Clayey varieties are likely to represent sediments of probably tidal currents.

The Givetian rocks mark a new stage of the sea transgression onto the East European Platform. The

sedimentation area extended eastward, to the Kotel'nich Arch. However, extremely shallow-water monomictic sands that accumulated there and mixed organic remains suggest the existence of a syndimentary uplift. According to data obtained in the course of previous studies, clastic products were mainly derived from the north, i.e., the Baltic Shield. Tikhomirov reckons that the Givetian Basin was filled with freshened water, and sediments of the northern part of the Moscow Syncline accumulated under conditions of a submarine delta (Tikhomirov, 1995).

The currently available evidence suggests that the sedimentary pile varied from 40 m in the first and fifth structural–facies zone (the Kubenskaya and Pyshchug boreholes) to 250 m in the second structural–facies zone (the Soligalich Borehole). Abrupt and often contrasting changes in the thickness were probably associated with movements of platform basement blocks. Such a viewpoint was proposed earlier as well. In par-

ticular, the activation of the Central Russian (Soligalich) Aulacogen in the Riphean as well as the subsidence by 200 m (Tektonika..., 1991) were also reported. Our studies allow us to reveal some new regularities (Figs. 3, 4).

The analysis of the thickness of the Givetian rocks makes it possible to establish the changes in the structural pattern of the basin compared to those in the Eifelian. Troughs above the Aulacogen are of inherited nature. Though scarps along the Vologda and Tot'ma faults formed in the Givetian. This is confirmed by sharp thickness differences on either sides of the faults. The subsidence of the graben of the Central Russian Aulacogen was also inherited, but more intense and contrasting subsidence took place in the Givetian. The phenomena had little effect on the Kresttsy Aulacogen. Hence, the subsidence in the Central Russian Aulacogen is related not to the common tension of the platform body, as it was inferred earlier (Tektonika..., 1991; Nikishin *et al.*, 1996), but to differentiated strike-slips along faults, which bounded aulacogens, and along the Rybinsk transverse fault zone, resulting in the formation of both tension zones and compression zones. This viewpoint is supported by the formation of a transverse uplift along the Rybinsk Fault where the thickness of Givetian sediments reduced from 150–170 m to 108–111 m in the Givetian (Figs. 4, 5).

As a result of the differentiation of structures within the Galich Depression, the uplift, which existed there during the late Emsian and Eifelian, was divided into two blocks separated by a trough along the eastern flank of the Rybinsk Fault along the Neya–Ivanovo profile (Figs. 4, 5). The northeast-oriented strike of the newly formed trough and its diagonal position with respect to faults bounding the Central Russian and Moscow aulacogens indicate the strike-slip nature of the structure.

The inherited development of the southern trough continued in the Givetian. Though the axis of the greatest subsidence migrated southwards at that time because of uplifting along the Rybinsk Fault to take up position between the Moscow Aulacogen and the Vyatka dislocation system. The Kotel'nich Arch formed as a synsedimentary uplift (the fifth structural-facies zone) since the Givetian.

## THE EARLY DEVONIAN

### *The Frasnian Age (The Early and Middle Frasnian Time)*

This time is characterized by a complete sedimentation cycle that started as the largest (in the Devonian) sea transgression in the early Frasnian after the structural pattern rearrangement in the Givetian. The beginning of the transgression is distinguished for the prevalence of the terrigenous sedimentation. The maximal transgression marked by the dominant carbonate accumulation falls into the earlier half of the middle Frasnian (the Sargaev time). The end of the time interval is characterized by the growth of intrabasin uplifts, an increase in the terrigenous (mainly clayey) material influx, and the reduction of the carbonate accumulation area. This seems to be associated with a greater tectonic differentiation of the basin in the terminal middle Frasnian, a decrease in the basin area, and its general shoaling.

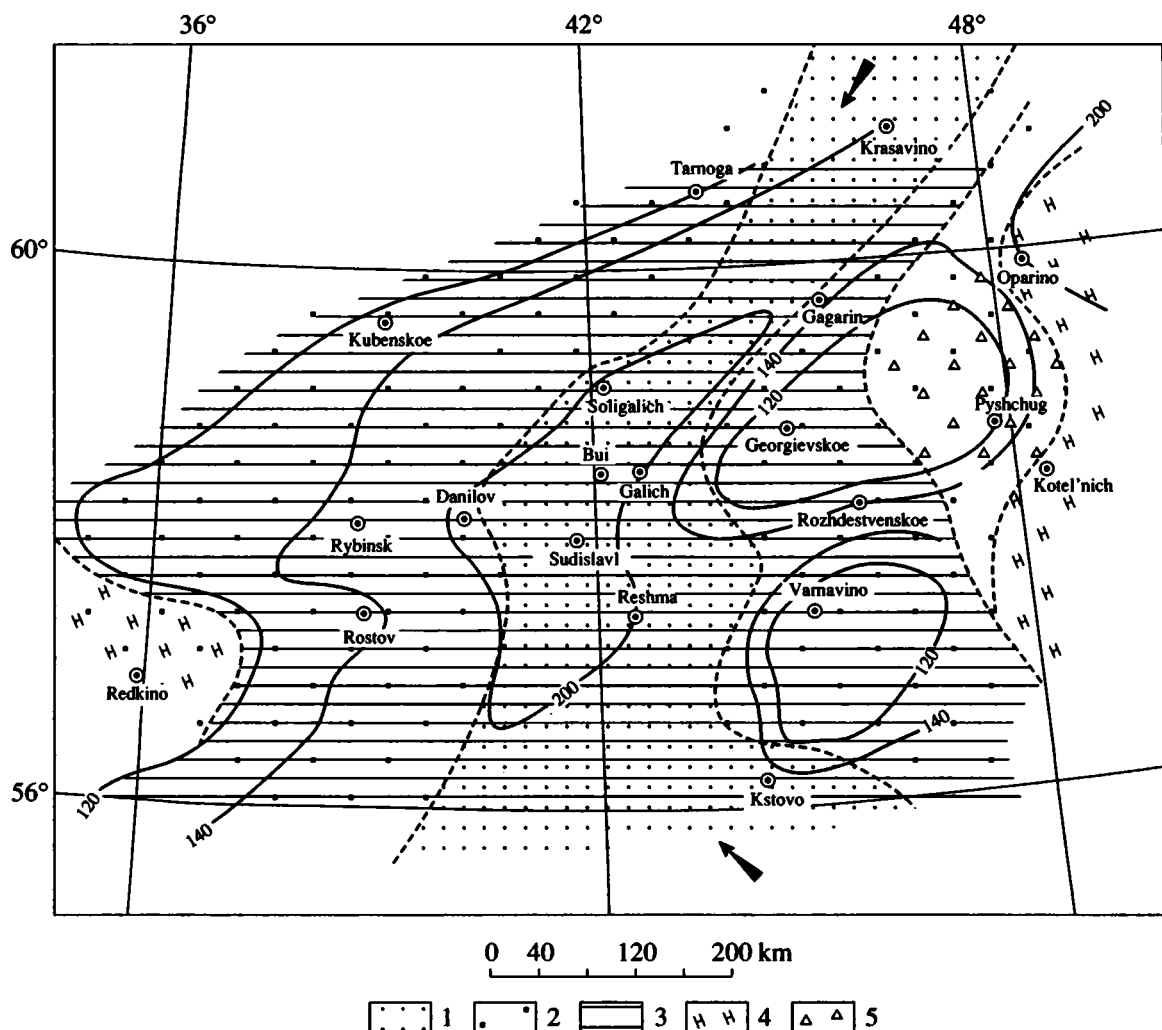
The early-middle Frasnian sea basin is characterized by five (sand-clay, sand, clay-carbonate, carbonate, and of carbonate breccia) facies (Fig. 6).

The early-middle Frasnian sea basin is characterized by five (sand-clay, sand, clay-carbonate, carbonate, and of carbonate breccia) facies (Fig. 6).

The **sand-clay facies** is typical of the section basement and sections with the maximal thickness (40–80 m). The facies infills an S-shaped and NE-striking depression evolving since the Givetian. It occupied the area above the Central Russian Aulacogen and the central part of the Galich Depression near Kostroma and Sudislavl (Fig. 6). A close alternation of variegated fine-grained quartzose sandstone, clayey siltstone and silty clay is characteristic of the facies. A poor differentiation of the sandy and clayey material, the presence of carbonified plant remains, as well as cross-laminated structures, including the flow-type structure (e.g., in the Kstovo Borehole), are also typical of the facies. These specific properties suggest that the sediments were accumulated under conditions of subsidence and fast burial of sediments. It is conceivable that a clinoform or a submarine alluvial fan could exist, the maximum thickness of which falls into the axial part of the Central Russian Aulacogen. Clastic products are likely to be derived from the northeast, although some part of them, especially clayey material, undoubtedly was brought from the local intrabasin rises and the southern Tokmovskoe Rise. This assumption is confirmed by the increase in the sandstone content in the Kstovo Borehole and by the presence of terrigenous rocks with cross-laminated flow-type structure on the territory.

The **sand facies**, 10–60 m thick, is also typical for the base of the early-middle Frasnian sedimentation cycle. However, it started to form a little later than the sand-clay facies during the expansion of the transgression (in areas occupied by the sand facies, the lower Frasnian rocks have a narrower stratigraphic range due to the absence of lower members). Light-colored, washed out, and well-sorted quartzose sandstones with scarce cement are most typical of the facies. Siltstone and clay interlayers are rare and thin. A high content of accessory minerals, zircon, sphene, and tourmaline included, was noted. These peculiar features indicate conditions of repeated roiling and rewashing of sediments under the shallow-water and active hydrodynamic conditions. The underlying Givetian sediments were also partially washed. Most likely, the facies characterizes shoals of intrabasin rises with relatively slow subsidence.

The **clay-carbonate facies**, 30–70 m thick, overlies the terrigenous rocks described above. The facies contains pelitomorph (calcilutite) gray and dark gray



**Fig. 6.** The facies-paleogeographic scheme for the early-middle Frasnian. (1) Submarine fan (sand-clay facies); (2) shoals of intra-basin rises (sand facies); (3) littoral zone with intense subsidence (carbonate-clay facies); (4) intrabasin rises (carbonate facies); (5) slopes of intrabasin rises (carbonate breccia facies). See Fig. 2 for other symbols.

limestones, clayey limestone and marl which comprise dark gray and greenish gray clay interlayers. The clay content increases upwards. Some varieties are dolomitized and rarely anhydritized. Moreover, a slight silicification of carbonate rocks was noted in the Central Russian Aulacogen. Thin-laminated and microlaminated structures indicating the significance of currents for the accumulation and redeposition of sediments are typical of the facies. Washout surfaces and nondepositional hiatuses (the Georgiev Borehole) were revealed in some areas of intrabasin rises. Sediments comprise remains of once abundant stenohaline fauna of brachiopods, echinoderms, and ostracods. Organic remains are irregularly distributed in sediments, often being of poor preservation probably due to redeposition by currents. The lifetime accumulation of organic matter is only confined to occasional small lenses. Peculiar features of the sediments indicate the abyssal environment, subsidence, and inadequate compensation by

sedimentation. The greatest thickness of the sediments is registered in the central depression near Sudislavl and Soligalich (Fig. 6).

The **carbonate facies**, 70–190 m thick, is developed on intrabasin rises (within the Kotel'nich Arch) and in the vicinity of Tver (Fig. 6). Light gray, organogenic, organogenic-detrital, oncolitic limestones, and calcarenites, practically barren of a clay admixture, are typical of the facies. The limestones are rich in diverse fauna remains, as a rule of good preservation. Echinoderms, corals, and algae are abundant in addition to brachiopods. Besides shell fragments, calcarenites comprise coprolites, as well as oolites and enveloped grains. Peculiar features of the facies indicate that it accumulated in a shallow-water zone of a higher biologic productivity, most likely, on submarine banks and intrabasin shoals with separate bioherms and calypers of algae, which were protected against the influx of the terrigenous material. A large thickness of these sedi-



ments indicates that the zone subsidence was completely compensated by sedimentation.

The **carbonate breccia facies** is confined to the western part of the fifth structural-facies zone (near Pyshchug). It characterizes the slope of the carbonate platform of the Kotel'nich Arch. The facies comprises dark-colored pelitomorphic limestones with fragments of thin-walled shells. The carbonates are similar to those in the clayey-carbonate facies and contain breccia and submarine slump horizons. Breccia represent clayey calcilutite with irregular dissemination of shell fragments, separate coprolites, worm tubes, as well as large (up to several centimetres) intraclasts of light-colored carbonate-facies limestone represented by calcarenites, oolitic, coprolitic and algal varieties. The matrix is locally crushed, indicating the slumping and flowing of a not fully consolidated sediment. A part of the intraclasts with unclear outlines was settled in the incompletely consolidated state. The amount of breccia decreases westward. The last thin interlayer was encountered in the Georgiev Borehole. The distribution pattern of the carbonate breccia facies indicates the existence of a slope or most likely a tectonic scarp along the western periphery of the carbonate uplift in the Kotel'nich Arch.

To sum up, we may infer that the sea basin, which existed on the territory of the Moscow Syncline in the early-middle Frasnian, was noted for normal salinity and rugged bottom relief. Sedimentation proceeded under conditions of general subsidence compensated by sedimentation to a different extent. This enhanced the contrast topography of the basin bottom that was mainly developed during the Givetian. The sea transgression proceeded most likely both from the northeast (in modern coordinates) and from southeast, i.e., the Uralian Paleoocean. In the beginning, depressions in the Givetian bottom topography were subjected to ingression and flooding, as is evidenced by different stratigraphic ranges of the lower Frasnian basal strata.

### *The Late Frasnian Time*

Depositional environments and specific properties of the paleogeography of the sea basin, which existed on the territory of the Moscow Syncline in the late Frasnian, could be inferred by sediments of the Don Superhorizon. Their deposition was preceded by the structural rearrangement of the platform manifested in activation of faults that bounded the eastern slope of the Voronezh Anteclise. Lava flows are evidence in favor of the tectonic activity as well (Rodionova *et al.*, 1995). Changes in strikes of facies zones also provide support for the structural rearrangement of the territory discussed. The facies zones were extended in the north-eastern direction in the early-middle Frasnian (Fig. 6) and in the sublatitudinal direction in the late Frasnian (Fig. 7). It is probably related to displacements along faults that bound the Central Russian Aulacogen. A

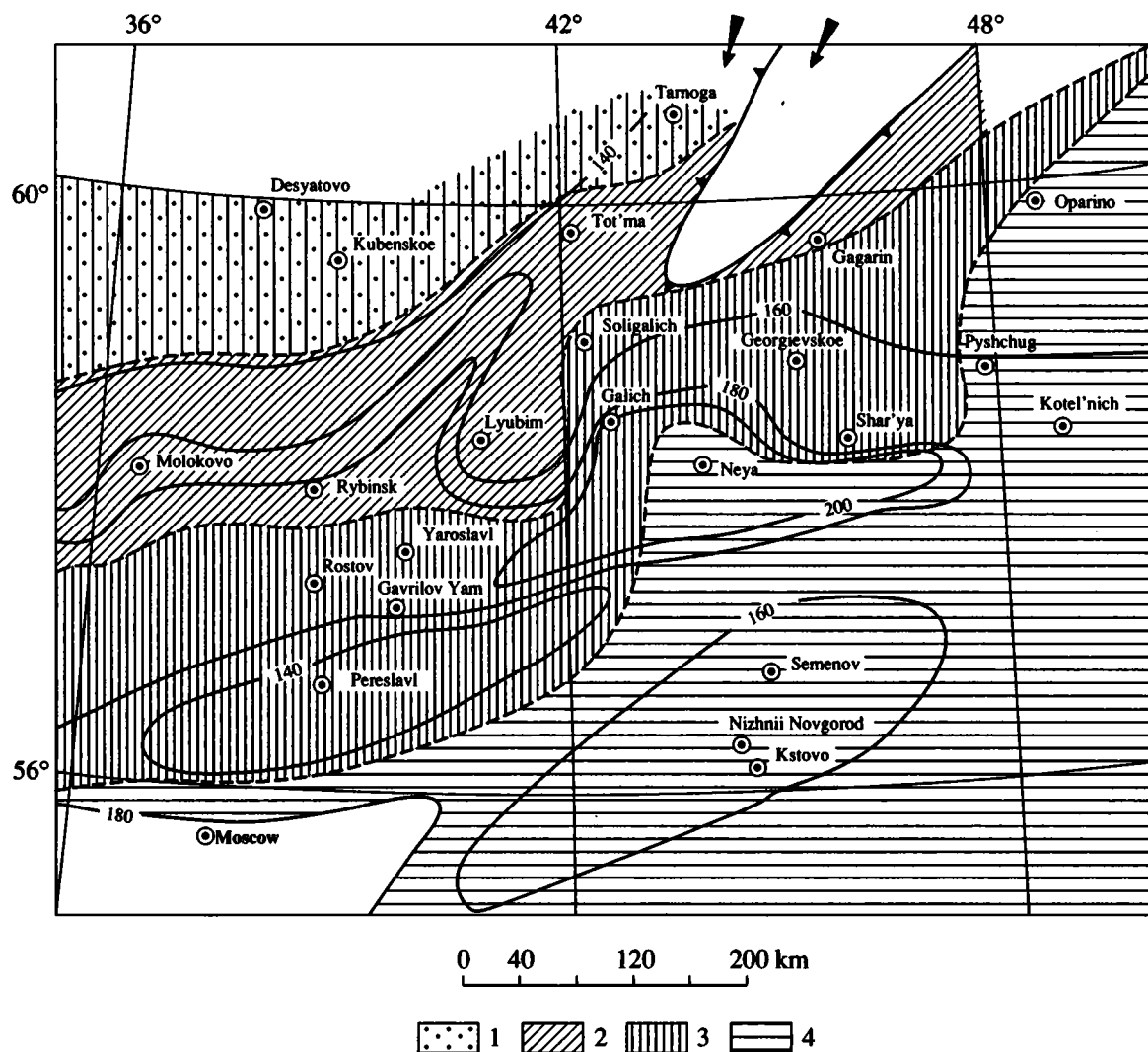
gradual inversion of the Central Russian Aulacogen at the end of the Frasnian confirms it.

The upper Frasnian rocks transgressively overlap the eroded surface of the middle Frasnian sediments and indicate an independent sedimentation cycle. Being developed throughout the whole region, the rocks were completely washed out at a later time in the extreme northeast in the vicinity of Roslyatino. The upper Frasnian rocks are represented by a variable terrigenous-carbonate association, 100–230 m thick. They can be divided into the clay-sand, sand-clay, carbonate-clay, and carbonate facies.

The **clay-sand facies**, less than 100 m thick, occurs in the lower part of the section, mainly in the northernmost part, within the first structural-facies zone. The facies is made up of dominating fine-grained, quartzose sand and sandstone with siltstone and clay interlayers. Laminated, sometimes cross-laminated structures are characteristic of the facies. Upwards, the number of siltstone-clay interlayers increases, and sandstone, siltstone, and clay rhythmically alternate. Rare and thin horizons of marl and limestone with brachiopod remains appear in zones of transition to other facies. The light gray and grayish green sandstone and siltstone have a clayey (hydromicaceous) cement. Carbonate cement is rarely observed. Clastic products are poorly rounded. The hydromicaceous clay and mudstone are grayish green, gray, and brown. In places, they comprise carbonified plant remains. Common in clay are thin-laminated structures that stem from changes in the amount of silty and sandy admixtures as well as in the color. The facies characterizes shallow-water conditions of the late Frasnian sea transgression. The high clay content in sandy deposits indicates the washout of the underlying middle Frasnian sediments during the sea transgression. An active hydrodynamic regime may be assumed, as most of the clayey material was carried away into adjacent facies zones.

The **sand-clay facies** replaces the clay-sand facies in the southern direction, toward basin offshore areas. Clayey rocks sharply increase in abundance in the facies. Sandstone makes up only separate horizons, the number of which tends to grow downward the section. In contrast to the thickness of clay-sand facies, the thickness of sandy-clayey rocks abruptly builds up to 180 m. Thin-laminated, sometimes lenticular-laminated structures of clayey rocks indicate that most of them were deposited by flows. Separate clinoforms are not improbable. Changes in the amount of the silt influx as well as variegated colors of rocks suggest seasonal climatic fluctuations. Organic remains are represented by ostracods and conodonts. The facies characterizes deeper sea environments as compared to the clay-sand facies.

The **carbonate-clay facies**, 130–200 m thick, replaces purely terrigenous sediments, described above, in basin areas more remote from the terrigenous material provenance, as well as upward the section



**Fig. 7.** The facies-paleogeographic scheme for the late Frasnian. (1) Coastal shallow-water zone (clay-sand facies); (2) sea basin slope (sand-clay facies); (3) intensely subsiding littoral zone (carbonate-clay facies); (4) littoral zone of uncompensated subsidence (carbonate facies). See Fig. 2 for other symbols.

marking the onset of the transgression and expansion of the basin area. The presence of clay and marl with a variable amount of carbonate admixture is the most characteristic feature of the facies. Interlayers of purely terrigenous rocks become thinner and tend to the base of the facies. Interlayers of microgranular (micritic and calcilitic) limestone, clayey limestone, more rarely dolomitized limestone, and carbonate rocks with anhydrite clusters appear. The rocks mentioned are greenish gray (more rarely dark gray) and thin-laminated. The facies marks the intensely subsiding central parts of the basin with a limited influx of the terrigenous material. As a consequence, carbonate accumulation assumes a greater significance. The facies is characterized by a maximal thickness of sediments. A thin-laminated structure and abundance of rocks with different compositions indicate a great role of currents in the redeposition of sediments. Elements of the rhythmic alternation

of rocks with a variable amount of the terrigenous admixture indicate seasonal fluctuations of the climate. Processes of dolomitization and a weak anhydritization suggest a gradual increase in the climate aridity in the terminal Frasnian.

The **carbonate facies** is developed in the extreme southeast of the region (Fig. 7). Marl, limestone, and dolomite are typical of this purely marine facies. The facies appearance is determined by greenish gray pelitomorphic marls with a vague horizontal lamination, which comprise limestone or dolomite interlayers and lenses, 0.5 m thick. Upwards, the thickness of limestone interlayers increases up to 20 m. The gray and greenish gray, microgranular limestone contains a clay admixture, along with abundant and diverse stenohaline fauna (brachiopods, ostracods, crinoids, and others). Organogenic-detrital varieties are occasional. A

poor influx of terrigenous material from land and the prevalence of carbonate sedimentation resulted in the decrease in the sedimentation rate and rock thickness. The carbonate facies characterizes apparently subsidence areas in the littoral zone, which were compensated by sedimentation to the least extent. It may be suggested that the Kotel'nich Arch, as a synsedimentary uplift, was no longer existent at the end of the Frasnian.

Thus, the late Frasnian sea basin of the northeastern part of the Moscow Syncline was characterized by the sublatitudinal zonation; i.e., the amount of the terrigenous material brought into the basin decreased from the north-northwest to south-southeast. Clastic products were brought not only from the remote land. Middle Frasnian (the Semiluki age in the regional scale) clayey sediments were also subjected to substantial washout. The abundance of clayey material determined the thickness of sediments and, to a certain extent, the depth of sedimentation due to a variable rate of subsidence compensation by sedimentation. The second and third structural-facies zones served as areas for the terrigenous material discharge. Rhythmic changes in the amount of the terrigenous material, processes of dolomitization, and sometimes anhydritization indicate seasonal fluctuations of the climate and gradual aridization. The subsidence of the Kotel'nich Arch was a characteristic feature of the region.

### *The Famennian Age*

Following the break in sedimentation and a small-scale washout at the top of the upper Frasnian deposits in the northern part of the territory discussed, seawater again penetrated into the Moscow Syncline from the Uralian Paleoocean. A new sea basin existed until the terminal Famennian without remarkable structural rearrangements. A temporary reduction of the basin area took place only at the boundary between the early and middle Famennian. It was accompanied by a short-lived water retreat in the northern part of the region. After the regression, however, the sedimentation regime and paleogeographic environments within the Famennian basin substantially changed.

### *The Early Famennian Time*

That time-interval is characterized by an accumulation of clayey-carbonate rocks. The facies zonation is determined by the amount of terrigenous, mainly clay material. The rocks can be divided into three (silty-clayey, carbonate-clayey, and carbonate) facies (Fig. 7).

The **silt-clay facies** is typical of the northernmost part of the basin. Only in the neighborhood of Lyubim, Danilov, and Sudislavl, terrigenous rocks are protracted in the form of a lobe farther toward the center. Dominating among the rocks are mudstone-like (silty or dolomitic) clays with siltstone and sandstone interlayers in the lower part of the section. Clays are brown, greenish gray, and yellowish gray, have a thin-lami-

nated structure, and contain fossils of lingulids, fish bones, and carbonified plant detritus.

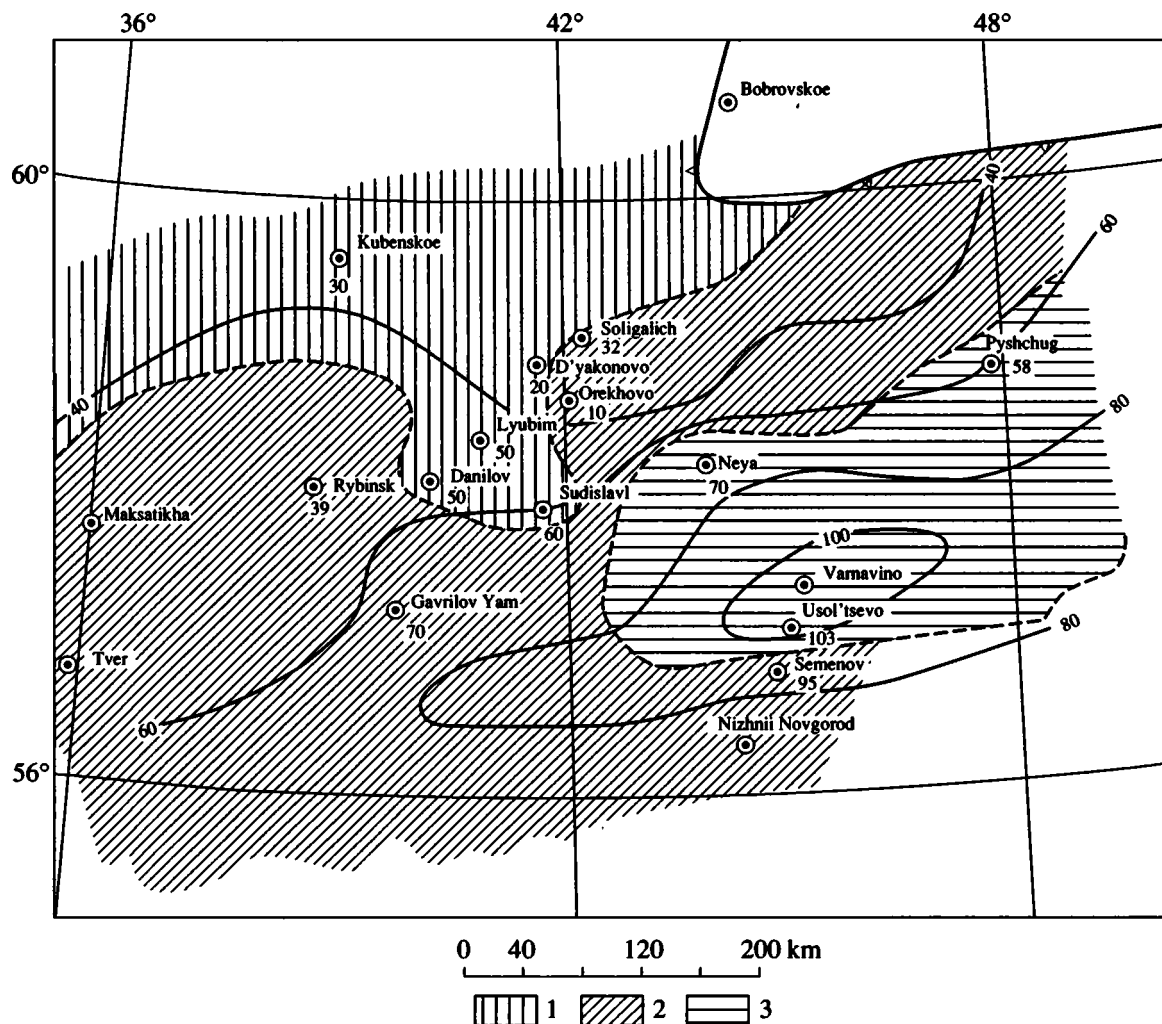
Siltstone and silty sands make up occasional, more often thin interlayers. They are most common near Lyubim, Danilov, and Sudislavl. Simultaneously, the thickness of deposits increases that allows us to distinguish a zone of the maximum unloading of terrigenous clastic products brought by currents and accumulated as a submarine fan or delta. Peculiar features of sedimentation described by Birina (1957) in the Lyubim Borehole favor this inference. She found there silty sands and sandstones with dolomitic cement, which alternate with micro-laminated micaceous and silty clays. The clays include clusters of rounded, sorted, small fish bones, sometimes cemented by numerous glauconite segregations. Upward the section, sand and silt admixture decreases while interlayers of dark gray clay with carbonified plant remains oriented along the bedding appear. Silt grains are composed of quartz and feldspar (up to 22%). Thin dolomite interlayers, among which clastic varieties dominate, and even a horizon of dolomitic conglomerate appears in the upper part of the facies. The clastic carbonate material is represented by stromatopore fragments and oolites. Limestone with Charophyta fossils are also found in the facies.

The facies is likely to characterize shallow-water littoral areas in the basin with unstable water salinity and active hydrodynamics. Sometimes, the water freshening in the littoral zone probably took place and favorable conditions for charophytes were created. The presence of clastic carbonate material indicates that underlying Devonian and Silurian rocks were eroded.

The **carbonate-clay facies** replaces the silt-clay facies, partially upward, partially laterally in the southward direction (Fig. 8). A close alternation of beds of greenish gray clayey dolomite and greenish clays are typical of the facies. Massive dolomite layers separated by black, often bituminous clay interlayers are also present. As in the terrigenous facies, at least a part of dolomite is of clastic nature. Clays include fish bones. The facies probably represents much deeper parts of the basin bottom where clayey material was only sporadically supplied probably because of seasonal fluctuations of the climate. It may be inferred that calm conditions with stagnant phenomena dominated in the basin.

The **carbonate facies** is developed in the southeastern part of the basin. It is distinguished for the maximum thickness of the lower Famennian sediments. Taking into consideration a small amount of allochthonous terrigenous material in the rocks, we may assume that carbonate rocks were in the maximal subsidence zone and mark, most likely, the direction of the Famennian transgression.

Dolomitized limestones with a variable clayey admixture dominate in this facies. Marl interlayers are few as in the case of carbonate-clay facies found in the zone of transition to the carbonate-clay facies. Fauna fossils are rare and poorly preserved. The facies is char-



**Fig. 8.** The facies-paleogeographic scheme for the early Famennian. (1) Coastal shallow-water zone (silt-clay facies); (2) sea basin slope (carbonate-clay facies); (3) sea basin depression (carbonate facies). See Fig. 2 for other symbols. Isopachs are shown for the whole Famennian.

acteristic of a muddy depression with conditions favorable for a simultaneous settling of thinly elutriated carbonate and clayey material. Poor organic fossils and processes of dolomitization suggest a stagnant regime in the depression.

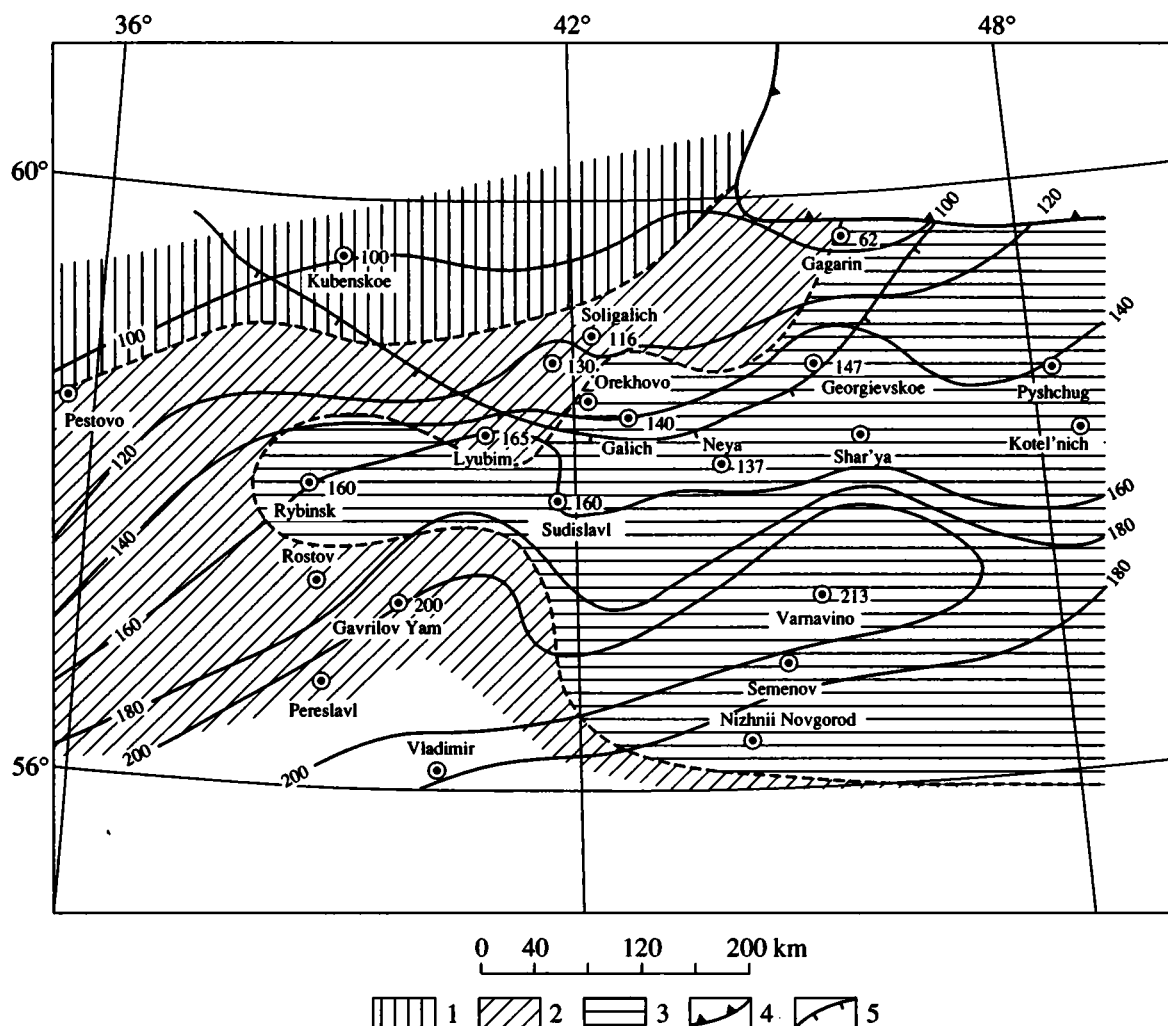
Thus, we may infer that a sea basin with the sedimentation of clayey-carbonate material existed at the region in the early Famennian. Isolated depressions within the region created favorable conditions for stagnation.

#### *The Middle and Late Famennian Time*

Sedimentation at that time interval proceeded after a small-scale reduction of the Famennian basin area and a partial erosion of early Famennian sediments in the northern part of the territory. A new basin expansion in the middle Famennian resulted in accumulation of gypsiferous sediments. In the northeastern area, the

upper part of rocks was washed out in the Carboniferous. Carbonate-clayey and clayey-carbonate sediments with abundant sulfates dominate. They comprise separate interlayers and lenses of gypsum and anhydrite. The maximum development of halogenic facies falls within the earlier half of the time interval. The morphology of middle-late Famennian basin and the dependence of the composition of sediments on the abundance of the allochthonous terrigenous material are inherited since the early Famennian. It is possible that a part of the facies features has not been revealed because of a scarcity of core material. Rocks of this time interval can be divided into four (clay, anhydrite-bearing, carbonate-clay, anhydrite-bearing carbonate, and limestone facies).

The **clay facies** is developed in the northern part of the region discussed. Clayey, thinly laminated and marly sediments with anhydrite and dolomite interlayers in the middle part dominate there. Compositionally,



**Fig. 9.** The facies–paleogeographic scheme for the middle and late Famennian. (1) Tidal zone of a salinating sea basin (clay facies); (2) slope of a salinating basin (anhydrite-bearing carbonate–clay facies); (3) salinating sea basin (anhydrite-bearing carbonate facies); (4) boundary of recent sediments; (5) boundary of the recent distribution of the upper Famennian sediments. See Fig. 2 for other symbols. Isopachs are shown for the whole Famennian.

clays are similar to the early Frasnian sediments, though almost do not contain sandy and silty admixture. The facies characterizes littoral sectors of a shallow-water basin, probably within the tidal current zone.

The **anhydrite-bearing carbonate–clay facies** replaces the previous one in a northward and southwestward directions (Fig. 9). It is represented by alternating layers of yellow–brown dolomite, dolomitic marl, dolomite–anhydrite, and clay. A thin horizon of dolomitic conglomerate that marks the washout surface of underlying rocks can be encountered sometimes at the section base (the Lyubim Borehole). Dolomites consist of a fine intercalation of microgranular carbonate with clastic carbonate that makes up more solid interlayers. They give way to sulfatized dolomites. In other areas, dolomites are clayey, fine-grained, and pelitomorphic. They often grade into gray, yellowish brown, and dark brown mudstone with fine-laminated

horizontal structures and thin (up to 1.5 cm) anhydrite interlayers.

The **anhydrite-bearing carbonate facies** is distinguished in the southeastern part of the territory discussed. Dominating dolomites contain rare interlayers of dark green and greenish gray clay and silty clay. Birina (1957) reported the prevalence among dolomites of clastic varieties with anhydrite clusters, sometimes with fluorite cubicles, as well as small and large dolomite pebbles. They alternate with greenish gray clayey dolomites with a glassy appearance owing to anhydrite impregnation. Sometimes, dolomites contain surfaces that bear witness to a partial or complete dissolution of sulfate layers. Such surfaces found along with clastic dolomites indicate sealevel changes, the alternation of flooding periods in combination with a decrease in the water salinity and dissolution of sulfate sediments, as

well as periods of drying up, roiling of sediments and their redeposition under shallow-water conditions.

All the late Famennian sulfate-bearing deposits described are noted for intense post sedimentary transformation of rocks. Sedimentary structures in them are often shaded by diagenetic processes of carbonate migration, transformation of manganocalcite into dolomite, and penetration of anhydrite into the layers. Primary dolomite is hard to distinguish from diagenetic one. All specific properties mentioned above are typical of salinating lagoons as well as closed and semiclosed basins with a higher water salinity.

The **limestone facies** is confined to the uppermost Famennian. It marks the enhanced water circulation, decrease in water salinity, and disappearance of conditions for sulfate accumulation. Shallow-water limestone with fragments of ostracods and charophytes becomes characteristic.

Thus, a shallow-water basin, sometimes drying up in part, with a high water salinity and sedimentation typical of the early phase of the evolution of halogenic sea basin existed on the territory of the Moscow Syncline in the later half of the Famennian.

## CONCLUSIONS

Data on the facies and the basin analysis allow us to trace the Devonian history of water basins at the territory of the Moscow Syncline on the East European Platform. Seven sedimentation cycles in the region resulted from periodic sea transgressions and regressions on the syncline territory, as well as structural rearrangements due to the evolution of oceanic basins surrounding the East European Platform at that time.

Early Devonian transgressions in the Moscow Syncline advanced from the Baltic shelf basin of the Caledonian Yapetus Ocean. The closure of the paleocean in the earliest Devonian resulted in uplifting, as well as a prolonged hiatus that lasted from the later half of the Lochkovian to the Pragian and the earlier half of the Emsian. The sea basin emerged there only in the late Emsian and Eifelian. It was still connected with the Baltic basin, although it was separated by a system of intrabasin rises. In the Middle Devonian, the sea transgression proceeded from the opening Uralian Paleoocean. The Caledonian orogeny was manifested in the influx of terrigenous material from the Baltic Shield. This resulted in formation of a basin with a high water salinity that was similar in the sedimentation type to basins of intermontane orogenic depressions. The basin topography in the Eifelian was governed by subsidence and probably tension in Riphean aulacogen zones (Orsha-Kresttsy, Central Russian, and Vyatka). The Kotel'nich Arch occupied the highest position at that time and, therefore, was eroded.

The terrigenous sedimentation dominated in the basin in the Givetian as well. A substantial rearrangement of the Moscow Syncline occurred in the

Givetian, most likely during the Tel'bes orogenic phase. Dominating in the basin was terrigenous sedimentation with abrupt changes in the thickness of deposits, which indicated active tectonic movements. Displacements caused by the rotation of the Volga-Urals megablock of the basement with respect to the Fennoscandian megablock prevailed. The Pyshchuga Fault, which bounded the Kotel'nich Arch on the west, probably formed at that time. The structural rearrangement in the Givetian resulted in substantial changes in the structural-facies zonation. As a consequence, the Moscow Syncline was subjected to a major sea transgression from the Uralian Ocean to form a deep basin with diverse stenohaline fauna and substantial carbonate sedimentation. The basin existed until the latest Devonian. A short-term regression happened only at the end of the middle Frasnian. A new structural rearrangement of the Moscow Syncline, as well as a general subsidence of the Volga-Urals basement megablock (the Kotel'nich Arch included), relative to the Fennoscandian megablock took place at the same time. Consequently, the NE-oriented strike of structural-facies zones was replaced by the sublatitudinal one with a general southward inclination. The climate turned into arid at the end of the Frasnian and the basin gradually grew shallower. The shallowing lasted through the Famennian and resulted in salinization and formation of a halogenic basin.

The Kotel'nich Arch was elevated above the water surface and served as a clastic material provenance during the Emsian-Eifelian. In the Givetian-middle Frasnian, the arch represented an intrabasin rise with a shallow-water sedimentation and bioherm structures. The entire structure began plunging at the end of the Frasnian.

The study carried out allows a conclusion on the structural nonuniformity of the basement of the East European Platform and differentiated strike-slip displacements of the basement blocks in the Devonian. The displacements governed the sedimentary cover structure and fault dislocations within the platform. The largest and long-lived faults (the Rybinsk and Pyshchuga faults, as well as faults bounding the Riphean aulacogens and passing into the sedimentary cover of the syncline) could serve as channels for the degassing and intense circulation of groundwater during the activation period. A high rock cementation and a higher temperature mineralization would thus be expected along those faults. In some periods, such long-lived fault zones could serve as barriers for the intrastratal migration of hydrocarbon accumulations.

## ACKNOWLEDGMENTS

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## CHRONICLE

# The Second All-Russia Lithologic Workshop for Young Scientists

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Under the aegis of the Federal Specific Program *The State Support for Integration of Higher Education and Fundamental Science for 1997–2000* (FSP Integratsiya), the Second All-Russian Lithologic Workshop for Young Scientists was held in the Village of Melikhovskaya, Ust'-Donetsk district, Rostov region, on September 20–24, 1999. The workshop was dedicated to the 100th birthday of Prof. Ignatii Andrianovich Shamrai (1900–1980), DSc (Geol.–Miner.), head of the Department of Mineralogy and Petrography, Rostov State University, an eminent lithologist, Honored Scientist of the Russian Federation. The workshop attracted 35 specialists, including 4 academicians and corresponding members of the Russian Academy of Sciences (RAS), the Russian Academy of Natural Sciences (RANS), and the International Academy of Mineral Resources (IAMR), 10 DSc and 11 PhD holders. They represented seven research, educational, and industrial production institutions of the Russian Academy of Sciences, the Ministry of Higher Education, and the Ministry of Natural Resources of the Russian Federation located in Moscow, Rostov-on-Don, Novocherkassk, and Essentuki.

Co-chairmen of the Organizing Committee of the workshop were Prof. V.I. Sedletskii, Academician of the RANS, the First Deputy Chairman of the Council of the North-Caucasian Scientific Center for Higher School, as well as Prof. N.I. Boiko, Academician of the IAMR, the Head of the Department of Mineralogy and Petrography, Rostov State University (RGU). The Scientific Secretary was O.S. Ponomarenko from the RGU.

Participants of the workshop were greeted at the opening ceremony by V.I. Sedletskii and N.I. Boiko, A.T. Ushak, the pro-rector of the RGU, P.P. Ul'yanov, the chairman of the Committee on Natural Resources for the Rostov region, and M.M. Kurbanov, chief geologist of the North Caucasian Regional Geological Center.

Twenty-four papers were presented and discussed at six sessions. A geological excursion was devoted to the inspection of the Paleozoic and Cenozoic geological section in the eastern Donetsk Basin (Donbas).

Key papers were focused on following problems:

(1) fundamentals of the theory of lithogenesis, the study of facies, and the facies analysis;

(2) the study of metallogeny of sedimentary formations in the context of new data on their structure, composition, and formation conditions;

(3) the geochemistry of sedimentary rocks;

(4) methods of studying sedimentary formations and related mineral deposits; and

(5) the association of lithogenesis with tectonics.

Fundamentals of the theory of lithogenesis, the study of facies and the facies analysis were considered in presentations by E.E. Karnyushina (MGU, Moscow), N.S. Skripchenko (YuRGU, Novocherkassk), V.A. Eroshchev-Shak (GIN, Moscow), M.M. Ryshkov (RGU, Rostov-on-Don), A.G. Granovskii (RGU, Rostov-on-Don), E.M. Pushkarskii (RGU, Rostov-on-Don), A.V. Zaitsev (Committee of Natural Resources for the Rostov region, Rostov-on-Don).

Problems of studying the metallogeny of sedimentary rocks in the context of new data on their structure, composition, and formation conditions were elucidated in papers by N.I. Boiko (RGU, Rostov-on-Don) and V.N. Trufanov (RGU, Rostov-on-Don).

The geochemistry of sedimentary rocks was considered in presentations by V.G. Popov (YuRGU, Novocherkassk), L.Ya. Kizil'shtein (RGU, Rostov-on-Don), M.Yu. Chernenko (YuRGU, Novocherkassk), I.I. Sendetskii (YuRGU, Novocherkassk), A.E. Khardikov (RGU, Rostov-on-Don), Yu.V. Agarkov (RGU, Rostov-on-Don), G.V. Zelenshchikov (GUP Yuzhgeologiya, Rostov-on-Don).

Methods of studying sedimentary formations and related mineral deposits were discussed in papers by L.Ya. Kizil'shtein (RGU, Rostov-on-Don), Yu.G. Maiskii (RGU, Rostov-on-Don), M.I. Gamov (RGU, Rostov-on-Don), S.I. S'yan (YuRGU, Novocherkassk), I.E. Stukalova (GIN, Moscow).

The association of lithogenesis with tectonics was considered in presentations by B.A. Sokolov (MGU, Moscow), B.P. Zolotarev (GIN, Moscow).

Presentations by young specialists and post-graduate students—O.S. Ponomarenko, I.A. Kholodnaya, A.V. Nastavkin, D.I. Pirko, F.V. Meshchaninov (all from RGU, Rostov-on-Don), A.A. Butenkov, E.V. Sukhanova, E.N. Glazyrin (YuRGU, Novocherkassk), L.I. Barchukova, O.O. Pivovarchuk (MGU, Moscow)—were discussed at the sessions as



well. The papers dealt with conditions of accumulation of the Mesozoic and Paleozoic sediments of the Russian Platform and Greater Caucasus. The use of sedimentary rocks as a multipurpose raw material, geochemical features of the origin of sedimentary rocks of different types, as well as other topical problems of lithology were considered.

In the course of discussions, the participants recognized the study of facies and the facies analysis, as well as the problems of the geochemistry and metallogeny of sedimentary rocks to be the topics of first priority in lithology.

The resolution adopted at the workshop points out that the basic task implying the strengthening of scientific communication between leading lithologists and young specialists has been fulfilled. It emphasized the

current state of the lithologic science, directed the trends of further investigations, and pointed out that annual lithologic workshops held in Russia undoubtedly contributed to the integration of higher education and fundamental science. The resolution expressed regrets at the fact that not all the lithological schools existing in the Russian Federation were represented at the workshop.

The Second All-Russian Lithological Workshop for Young Scientists recognized it appropriate to set up special courses at geological faculties of institutes, which have the lithologic specialization, for more thorough and purposeful studies of laboratory methods applied in lithology. The Third All-Russian Lithological Workshop for Young Scientists is proposed to be held in 2000.

## CHRONICLE

# The 70th Birthday of Evgenii Fedorovich Shnyukov, Academician of the National Academy of Sciences of Ukraine



Professor Evgenii Fedorovich Shnyukov, DSc (Geol.–Miner.), Academician of the National Academy of Sciences of Ukraine and the International Academy of Sciences of Eurasia turned 70 years old, along with 47 years of his creative scientific work, on March 26, 2000.

Shnyukov's scientific activity is comprehensive and ample in terms of geological problems and represents a brilliant example of a fruitful combination of science and practical work. In Ukraine, his name is closely related to the onset of a new stage in studying sedimentary iron and manganese ores, the geology of the Black and Azov seas, especially the Black Sea shelf, comprehensive geological–geophysical and metallogenic studies of the World Ocean floor.

Shnyukov made first steps in science in the Institute of Geological Sciences, the National Academy of Sciences of Ukraine, as a post-graduate student studying the mineralogy of the Krivoi Rog iron ore basin. He

wrote his first monograph *Ore Minerals of the Krivoi Rog Iron Ore Belt* in collaboration with Yu. Yu. Yurok. His work on martite deposits and processes of magnetite martitization is still of great interest.

During the ensuing years, Shnyukov took an interest in the Kimmerian Azov Sea–Black Sea iron ore province. Intense studies of the geology, mineralogy, and geochemistry of iron and manganese ores of the province, along with simultaneous studies of manganese ores of the Nikopol Basin, allowed him to elaborate a hypothesis on the formation of oolite and pseudo-oolite ores, to determine the decisive importance of the hydrodynamic activity of the sea for material differentiation in the sedimentary ore genesis. Based on theoretical predictions, he discovered several iron ore deposits in the Kerchenskii Peninsula, as well as revealed the relationship between some deposits (for instance, Novoselov deposit and others) and the mud volcano activity.

Investigations pertaining to the geology of shelves of the Black and Azov seas were of great interest for the geological theoretical and practical work. The first stage of the investigation resulted in the publication of an eight-volume monograph which, in addition to the geological structure and mineral resources, covered the stratigraphy, tectonics, lithology, and geochemistry of rocks in the shelf and adjacent areas of the continent and continental slope, as well as the geology of the Black Sea brackish lagoons and the Kerchenskii Strait. The creative work of Shnyukov as the organizer, chief editor, and co-author of such an interesting and fruitful monograph, as well as his team of researchers, were awarded the State Prize of the USSR in 1989.

Studies on the geology and mineral resources of the shelf, continental slope, and deep-water basin of the Black Sea are currently in progress. Despite economic problems, cruises of research vessels *Akademik Vernadsky* (1989, 1992), *Ikhtiandr* (1992–1993), *Mikhail Lomonosov* (1989), *Professor Vodyanitsky* (1994) were carried out under the supervision and with the direct participation of Shnyukov. Of special success were seven cruises of R/V *Kiev* (1995–1997), during which sapropel, sand, ferromanganese nodules were studied. The Lomonosov Massif of crystalline rocks was revealed. Hundreds of gas seepages were encountered, indicating the presence of oil and gas. The gold potential of old and recent sand placers were assessed. These studies resulted in the publication of tens of monographs. He is the author, co-author, and editor of more

than 200 scientific and popular-scientific works. Books published recently, such as *The World of Minerals, Treasures and Mysteries, Catastrophes in the Black Sea*, and others, gained wide recognition among readers and became rarities.

Shnyukov contributed much in the geology and metallogeny of the World Ocean. In parallel with studying the geological features of major tectonic structures, along with the petrography and endogenic metallogeny of ridges and rift zones of the Indian and Atlantic oceans, he gave considerable attention to ferromanganese nodules that are promising both in the scientific and commercial aspects. He was the first to formulate the notion "nodule field" and emphasize the genetic and commercial importance of stratabound nodules. He revealed and studied the influence of endogenic processes on the formation of nodules and confirmed the sedimentary-diagenetic origin of nodules. He repeatedly posed the question about the necessity of the Ukrainian participation in studies of the World Ocean (and, particularly, in all international organizations engaged in the prospecting and exploration of ferromanganese nodule areas), as well as the allotment of such an area for Ukraine.

Being a pioneer in studying marine geology in the Ukraine, he set up the school of marine geology. Tens

of post-graduate students, who successfully defended PhD dissertations under his scientific supervision, are currently working in science and industry and translating their teacher's ideas into life.

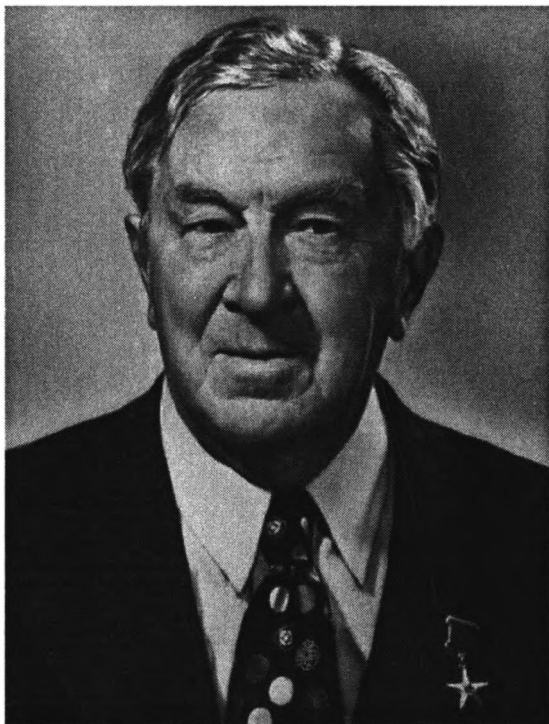
Shnyukov is engaged in tremendous organizational and scientific work. He was the director of the Institute of Geology from 1977 to 1992. Since 1992, he has worked as director of the Division of Marine Geology and Sedimentary Ore Genesis of the National Academy of Sciences of Ukraine (DMGSOG); director of the Museum of Natural History, NASU; head of the Department of Sedimentary Ore Genesis, NASU; chairman of the Museum Council, NASU; chairman of the Council on the Geology of Seas and Oceans; chairman of the Lithological Committee, NASU; and member of many other scientific councils and editorial boards of scientific journals.

With all our hearts, we would like to wish Shnyukov, a man of prodigious erudition and tremendous organizational talent, many years of creative life and new great successes in fruitful activity.

**Editorial Board of the Journal  
*Lithology and Mineral Resources***

## CHRONICLE

### In Memory of Aleksandr Leonidovich Yanshin



Academician Aleksandr Leonidovich Yanshin, an eminent scientist, a man of prodigious erudition, naturalist, and distinguished specialist in the field of Earth sciences, passed away in his 89th year in Moscow on October 9, 1999.

The Russian scientific community suffered a severe bereavement. We have lost a highly experienced field geologist, discoverer of many mineral deposits, gifted investigator of nature, and outstanding organizer of science.

Yanshin was born on March 28, 1911 in the family of a lawyer in Smolensk where he finished a ten-year specialized experimental school. He decided to give up his life to geology after moving with the family to Moscow. In 1929, he joined the School of geological collectors at the Research Institute of Fertilizers. After completing the one-year course in the same year, he started to work at the institute first as a junior geologist, then as a geologist and chief of a geological team. The institute, which was named in 1933 after the famous Russian Scientist Ya.V. Samoilov and became known as Research Institute of Fertilizers, Insecticides, and Fungicides, was at that time one of the key scientific institutions in our country. Investigations here were aimed

at studying and searching for sedimentary mineral deposits, mainly mineral fertilizers (phosphorite and potash salt). It is, therefore, not surprising that Yanshin maintained his interest to mineral fertilizers for the rest of his life. He always gave much attention to studying formation conditions and regularities of phosphorite, salt, and potassium deposit occurrence in the Earth's crust as well as their prospecting.

In 1936, he joined the Geological Institute, Academy of Sciences of the USSR, as a senior researcher and, later, the Laboratory of Regional Tectonics for many years (from 1956 to 1982). In 1937, he was awarded the PhD degree (Geol.-Miner.). In 1953, he was awarded the DSc degree for the dissertation *Geology of the Northern Aral Region*. That period of his scientific and practical work was very fruitful. His gift of profound investigation into nature was displayed to a full measure. His immense working capacity, irrepressible keenness for collecting new evidence, and persistent strive to generalization and comprehensive analysis allowed him to contribute significantly to studying the geology of the northern Caspian Depression, southern Urals, Mudogzhary, Aral region, Turan Plate, Mangyshlak, and Tuarkyr. He became a leading specialist of the country on the regional geology of western Kazakhstan and southern Urals. He discovered bauxite deposits, the Aral iron ore basin, the Krivlev lignite deposit, the Dzhilyan potassium deposit, and vast artesian basins in arid regions of Kazakhstan.

In 1958, Yanshin was elected Member of the USSR Academy of Sciences; he moved to Novosibirsk where he was named Vice-director of the Institute of Geology and Geophysics, Siberian Division, the USSR Academy of Sciences. That period was noted for his outstanding scientific and scientific-organizational activity on creating research teams and arranging geological investigations in Siberia and Far East. At the same time, he continued his work with colleagues and disciples at the Geological Institute (Moscow). The series of fundamental geological overviews, carried out under his supervision, gained universal recognition. Worthy of note among these are *Tectonic Analysis of Thickness, Structure Types of Young Platforms in Eurasia, General Features of the Structure and Evolution of Young Platforms, The Tectonic Map of Eurasia*, the monograph *The Tectonics of Eurasia*, and the 15-volume issue *Evolution of the Relief of Siberia and Far East*.

Yanshin organized and supervised collective studies on prospecting for phosphorites and potash salt in Siberia and Far East. He actively guided such scientific problems as *Evolution of Sedimentary Rock Formation*

and Ore Deposition in the Earth's History, *The Geological Structure and Evolution of the Asian Continent-Pacific Ocean Transition Zone Within the Soviet Sector of the Pacific Belt*. He gave much force and energy to organization and conducting of international studies on the theme *Regularities of the Structure and Evolution of the Hercynian Fold Belts in Eurasia*, as well as on the international Project *Late Precambrian and Early Cambrian Phosphorites of the World*. He not only participated in the projects but was a scientific supervisor, brilliant organizer capable of making the free creative atmosphere in order to solve controversial problems and to complete collective studies successfully. His high prestige as a scientist stemmed also from his humane attitude to people, respect for opponents, benevolence, and a keen interest in all ideas, especially new and ingenious concepts.

One glowing example of such successful collective studies organized by Yanshin is the discovery of Nepa potash-bearing basin, the largest in the world, in eastern Siberia. At the beginning of work in Novosibirsk, he substantiated the possibility of the discovery of large potash salt deposits among Cambrian sediments in eastern Siberia. Enormous work was done by him on the creation of teams specialized in salts—geologists, chemists, drillers, technologists, geophysicists—in Irkutsk, Krasnoyarsk, Kansk, and Novosibirsk. He organized specialized expeditions to drill prospecting boreholes in search for potash salt on a vast territory from the Enisei Range to the Baikal region. Hundreds of deep boreholes were drilled in many target areas from 1962 to 1978. His prediction was confirmed by the discovery of the large Nepa potash-bearing basin in the northern Irkutsk region in 1978. Within the limits of the basin, the commercial-category potash salt reserves at the Nepa deposit were calculated and prepared for mining. The scientific prediction so brilliantly confirmed can be regarded as one of the remarkable geological discoveries of the 20th century.

Developing the inferences proposed by M.N. Altgauzen, B.M. Gimmel'farb, V.N. Kholodov, and other researchers, A.L. Yanshin emphasized implications of the Late Precambrian–Early Cambrian phosphorite formation epoch for the Siberian region. At present, this global epoch is generally recognized throughout the world and confirmed by the discovery of phosphorite deposits in Kazakhstan, the southern part of Eastern Siberia, Mongolia, China, India, northern Australia, Africa, and South America. Geologists have been confronted with a problem, i.e., to find out what biosphere changes on the Earth caused global processes of phosphorite accumulation in the Late Precambrian–Early Cambrian.

Yanshin's ideas on the evolution of sedimentary rock formation, paleogeographic environments, tectonic structures, orogenesis, water salinity in the World Ocean, atmosphere, and geophysical fields have gained wide acceptance among the geological community as

well. Results of those studies were summarized at the 27th Session of the International Geological Congress in 1984 in his presentation *Evolution of Geological Processes in the Earth's History*. He believed that geology would develop in the 21st century in accord with basic notions of the evolution of geological processes.

In 1982, Yanshin was elected Vice-president of the USSR Academy of Sciences, and, at the same time, he was appointed Director of the Institute of the Lithosphere. The sphere of his scientific and scientific-organizational activity considerably expanded. Problems of environmental protection, rational use of natural resources, and ecological safety measures in the country became his major preoccupation. His uncompromising stand in the issue of transferring part of water discharge of northern and Siberian rivers to the southern arid regions of the Soviet Union, as well as constructing the Volga–Chograi Channel, which could be fraught with soil salinization in western Kalmykia, is well known. His contribution to solving ecological problems of the Aral Sea, Aral region, the Crimean Atomic Power Plant, the Rzhev Water Reservoir, the Leningrad Dam, the Ragunsk Hydroelectric Power Station on the Vakhsh River in Tadzhikistan, Kara Bogaz Gol, and the Caspian Sea is inestimable.

There is no way of listing the whole range of problems and interests Yanshin was engaged in. Two aspects of his activity, though, received general recognition and put him among distinguished organizers of the science who developed the best traditions of the Russian school of naturalists. The first aspect, which he gave much consideration during all his creative life, involved editing and publishing. For many years, he took charge of the preparation of the editor's portfolio in the USSR Academy of Sciences and national academies. He took an active part in creating the Siberian Branch of the Nauka Publishing House. More than 500 monographs and essays about the life and creative work of distinguished Russian and foreign scientists were published in the series *Scientific and Biographical Literature* under his supervision. His contribution to publishing and popularizing the scientific heritage of V.I. Vernadsky, the Russian outstanding scientist, is of paramount importance. The publication of Vernadsky's complete works was pioneered by Yanshin.

Yanshin's major preoccupation in later years was concerned with ecological problems. His striking and topical scientific-popular works on ecology always aroused considerable interest in readers. He became a top-level ecologist in this country and was elected first president of the Russian Ecological Academy set up in 1993. His scientific heritage is enormous and diverse. He published more than 500 works, numerous reviews, essays, and articles in newspapers, gave many interviews, and spoke over the radio and TV. His lectures and talks were always well thought-out, logical, and easily understood. In polemics with colleagues, he was always respectful to opponents.

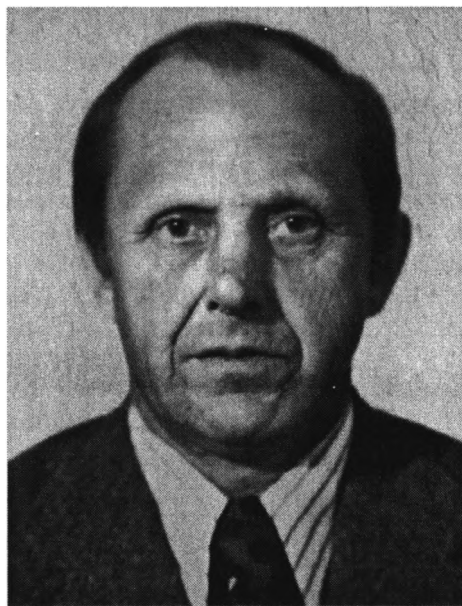
Yanshin's work as a specialist, scientist, and citizen was appraised many times by the government and scientific community. He was honored with many state awards, including the Hero of Socialist Labor, as well as academic and foreign prizes. He was a man of high culture, and splendid knowledge and prodigious erudition. He was noted for his patriotism, principles, a keen sense of justice, and a heartfelt kindness. He will forever remain in our hearts as one of the best representa-

tives of the Russian school of the geological science, an eminent scientist and naturalist of Russia.

**Editorial Board of the Journal  
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Interdepartmental Lithological Committee  
The staff of the Geological Institute,  
Russian Academy of Sciences**

## CHRONICLE

### In Memory of Ivan Sergeevich Chumakov



Ivan Sergeevich Chumakov, PhD (Geol.–Miner.), senior researcher of the Department of Lithology and Marine Geology, Geological Faculty, Moscow State University, an eminent scientist and excellent person, who took part in the Great Patriotic War, passed away on December 6, 1999.

Chumakov worked his hard way up at war and science. After finishing the secondary school in 1940, he was called up for military service, got the rank of an artillery-man, and fought at the Leningrad, Karelian, and Northern fronts until the end of the war. He was shell-shocked, decorated with Order of the Patriotic War (I grade), Medal for Courage, and other state awards.

After being demobilized in 1946, I.S. Chumakov entered the Moscow Geological Prospecting Institute and graduated in 1952. In 1952–1957, he worked in Rudnyi Altai as chief of a geological team in the Aero-geological Expedition (Aerogeologiya) and carried out the geological survey and stratigraphic analysis of the Cenozoic rocks. Thick loess–soil sediments, which are not amenable to stratigraphic subdivision, are typical of foothills in the region. On the basis of works by the Hungarian paleontologist M. Kretzoi (1942), Chumakov applied the method of separating and washing teeth of rodents and other smaller mammals. The teeth of animals appeared to respond very quickly to the change of paleogeographic environments; therefore, they represent an important stratigraphic marker. The strati-

graphic subdivision based on the change of mammal tooth types may extend hundreds of thousand years and allows distinguishing previously fauna-barren rocks.

Chumakov presented brilliant results of his stratigraphic studies in the monograph *The Cenozoic of Rudnyi Altai* (Trudy GIN, Moscow: Nauka, 1965). In 1964, he defended his PhD dissertation on the same topic under the supervision of M.V. Muratov, corresponding member of the USSR Academy of Sciences. The method of Chumakov has received wide recognition in Russia and has been highly successful.

In 1957–1959, he joined Expedition 23 (Gidro-proekt) as senior geologist and worked in Egypt carrying out the geological survey related to the construction of the Aswan Dam. Numerous boreholes drilled in the Aswan region showed that the depth of the Nile valley incision in the Pliocene reaches 1000 m and the valley is filled with transgressive clay and siltstone. He assumed that the level of the Mediterranean Sea in the Pliocene was still lower and, as the average depth of the sea is estimated to be 1500 m, the sea basin could dry up in the Late Miocene, turning into a deep arid depression filled with saliferous sediments. Such a “heretical” idea was given a hostile reception; many geologists dealing with the Quaternary geology in the Geological Institute, Russian Academy of Sciences (GIN) denied his assumption vigorously, especially, after the interview given by Chumakov to *The New York Times*.

However, subsequent drilling of deep boreholes in the Mediterranean Sea from R/V *Glomar Challenger* confirmed completely the correctness of his inferences. Ideas presented by him in the monograph *Pliocene and Pleistocene Sediments of the Nile Valley in Nubia and Upper Egypt* (Moscow: Nauka, 1967) became a truism at present. Nowadays, his assumption on the “Messinian Crisis” in the Mediterranean Sea is the subject of international seminars and symposia.

In 1972, after long-standing research work in Russia and abroad (Syria, Lebanon, Tunisia, Egypt), Chumakov joined the Department of Lithology and Marine Geology, Moscow State University. The stratigraphy, Cenozoic geology, and paleogeography of the Mediterranean Sea and eastern Paratethys commanded his attention there. Once again, he found a clue in the heap of complicated problems.

Volcanic ash interlayers, which represent good stratigraphic markers though hardly amenable to dating, are widespread in the Neogene–Quaternary sediments in the European part of Russia, Moldavia, Carpathian region, Crimea, and the Caucasus. Chumakov

applied a track method which allowed him to determine the absolute age of the interlayers and thus created the basis for precise correlation of events in different regions. The work resulted in monographs *The Earth's Crust and Evolution of the Mediterranean Sea* (Moscow: Nauka, 1981) and *Geochronology and Correlation of Late Cenozoic Sediments in the Paratethys* (Moscow: Nauka, 1992).

The creative work of Chumakov is difficult to depict in such a short paper. He was the author and co-author of more than 100 papers and monographs. Many of his ideas assumed their right place in the Russian science.

It should be noted that Chumakov was a generous person who easily gave out his assumptions, ideas, and

hypotheses to colleagues. These seeds are due to sprout, and we hope that a fond memory about him will remain for long in works by all researchers who communicated with this splendid person and scientist.

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